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US Patent App. No. 09/702,083

LIQUID DETERGENT COMPOSITIONS COMPRISING POLYMERIC SUDS ENHANCERS

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RELATED APPLICATIONS

This application is a continuation-in-part application of U.S. Application Serial No. 09/320,519 filed May 26, 1999, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

The present invention relates to liquid detergent compositions suitable for hand dishwashing comprising one or more polymeric suds volume and suds duration enhancers. The polymeric suds enhancers (suds boosters) suitable for use in the compositions of the present invention comprise cationic, anionic, and noncharged monomer units, or units having mixtures thereof, wherein said polymers have an average cationic charge density of 2.77 or less, preferably from about 0.01 to about 2.75, more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12. The present invention further relates to methods for providing enhanced suds volume and suds duration during hand washing.

BACKGROUND OF THE INVENTION

Liquid detergent compositions which are suitable for hand dishwashing must satisfy several criteria in order to be effective. These compositions must be effective in cutting grease and greasy food material and once removed, must keep the greasy material from re-depositing on the dishware.

The presence of suds in a hand dishwashing operation has long been used as a signal that the detergent continues to be effective. However, depending upon the circumstances, the presence of suds or the lack thereof, has no bearing upon the efficacy of liquid detergents. Therefore, the consumer has come to rely upon a somewhat erroneous signal, the lack or absence of soap suds, to indicate the need for additional detergent. In many instances the consumer is adding an additional amount of detergent far in excess of the amount necessary to thoroughly clean the dishes. This wasteful use of detergent is especially true in hand dishwashing since the soiled cooking articles are

usually cleaned in a "washing difficulty" queue, for example, glasses and cups, which usually do not contact greasy food, are washed first, followed by plates and flatware, and finally pots and pans which contain the most residual food material and are usually, therefore, the "greasiest".

The lack of suds in the dishwater when pots and pans are usually cleaned, together with the visual inspection of the amount of residual food material on the cookware surface, typically compels the consumer to add additional detergent when a sufficient amount still remains in solution to effectively remove the soil and grease from the dishware or cookware surface. However, effective grease cutting materials do not necessarily produce a substantial amount of corresponding suds.

Accordingly, there remains a need in the art for liquid dishwashing detergents useful for hand washing dishware which have an enduring suds level while maintaining effective grease cutting properties. The need exists for a composition which can maintain a high level of suds as long as the dishwashing composition is effective. Indeed, there is a long felt need to provide a hand dishwashing composition which can be use efficiently by the consumer such that the consumer uses only the necessary amount of detergent to fully accomplish the cleaning task.

SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in that it has been surprisingly discovered that polymeric materials having the capacity to accommodate a positive charge character, negative charge character, or zwitterionic character have the capacity to provide liquid hand wash detergent compositions with extended suds volume and suds duration benefits.

In one aspect of the present invention, liquid detergent compositions having increased suds volume and suds retention suitable for use in hand dishwashing, said compositions comprising:

a) an effective amount of a polymeric suds stabilizer (suds booster), said stabilizer comprising:

i) units capable of having a cationic charge at a pH of from about 4 to about 12:

provided that said suds stabilizer has an average cationic charge density of 2.77 or less, preferably 2.75 or less, more preferably from about 0.01 to about 2.75, even more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12;

b) an effective amount of a detersive surfactant; and

c) the balance carriers and other adjunct ingredients;

provided that a 10% aqueous solution of said detergent composition has a pH of from about 4 to about 12, is provided.

In another aspect of the present invention, liquid detergent compositions having increased suds volume and suds retention suitable for use in hand dishwashing, said compositions comprising:

a) an effective amount of a polymeric suds stabilizer (suds booster), said stabilizer comprising:

i) one or more units capable of having a cationic charge at a pH of from about 4 to about 12; and

ii) one or more units having one or more hydroxyl groups; provided that said suds stabilizer has a hydroxyl group density of about 0.5 or less, preferably from about 0.0001 to about 0.4; and

iii) optionally, one or more other monomeric units described hereinafter; provided that said suds stabilizer has an average cationic charge density of 2.77 or less units per 100 daltons of molecular weight; and

b) an effective amount of a detersive surfactant; and

c) the balance carriers and other adjunct ingredients;

provided that a 10% aqueous solution of said detergent composition has a pH of from about 4 to about 12, is provided.

In yet another aspect of the present invention, liquid detergent compositions having increased suds volume and suds retention suitable for use in hand dishwashing, said compositions comprising:

a) an effective amount of a polymeric suds stabilizer (suds booster), said stabilizer comprising:

i) one or more units capable of having a cationic charge at a pH of from about 4 to about 12; and

ii) one or more units having one or more hydrophobic groups, preferably the hydrophobic groups are selected from the group consisting of non-hydroxyl groups, non-cationic groups, non-anionic groups, non-carbonyl groups, and/or non-H-bonding group, more preferably the hydrophobic groups are selected from the group consisting of alkyls, cycloalkyls, aryls, alkaryls, aralkyls and mixtures thereof;

iii) optionally, one or more other monomeric units described

hereinafter;

provided that said suds stabilizer has an average cationic charge density of 2.77 or less units per 100 daltons of molecular weight;

b) an effective amount of a detersive surfactant; and

c) the balance carriers and other adjunct ingredients;

provided that a 10% aqueous solution of said detergent composition has a pH of from about 4 to about 12, is provided.

In still another aspect of the present invention, methods for providing increased suds retention and suds volume when hand washing dishware is provided.

These and other objects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

Additional background on these compositions and methods is provided by PCT Patent Application Serial Nos. PCT/US98/24853, PCT/US98/24707, PCT/US98/24699 and/or PCT/US98/24852 all incorporated herein by reference in their entirety.

All substituent groups in structural formulas in the Specification and Claims have the meaning defined in previous structural formulas in the Specification or Claims, respectively, unless indicated otherwise.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to polymeric materials which provide enhanced suds duration and enhanced suds volume when formulated into liquid detergent compositions suitable for hand dishwashing. The polymeric material may comprise any material provided the final polymers have an average cationic charge density of 2.77 or less, preferably of 2.75 or less, more preferably from about 0.01 to about 2.75, even more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12.

The liquid detergent compositions of the present invention comprise:

a) an effective amount of a polymeric suds stabilizer, said stabilizer comprising:

i) units capable of having a cationic charge at a pH of from about 4 to about 12;

provided that said suds stabilizer has an average cationic charge density preferably from about 0.01 to about 2.75, more preferably from about 0.1

to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12;

b) an effective amount of a detersive surfactant; and

c) the balance carriers and other adjunct ingredients;

provided that a 10% aqueous solution of said detergent composition has a pH of from about 4 to about 12.

It is preferred that the polymeric suds stabilizer (a) further comprises one or more of the following:

ii) one or more units having one or more hydroxyl groups,

provided that the polymeric suds stabilizer has a hydroxyl group density of ab about 0.5 or less, preferably from about 0.0001 to about 0.4 as measured by the Hydroxyl Group Density Equation as outlined in greater detail below; and/or

iii) one or more units having one or more hydrophobic groups,

preferably the hydrophobic groups are selected from the group consisting of non-hydroxyl groups, non-cationic groups, non-anionic groups, non-carbonyl groups, and/or non-H-bonding group, more preferably the hydrophobic groups are selected from the group consisting of alkyls, cycloalkyls, aryls, alkaryls, aralkyls and mixtures thereof.

It is desirable that the polymeric suds stabilizer (a) further optionally, but preferably comprises one or more of the following:

iv) units capable of having an anionic charge at a pH of from about 4 to about 12;

v) units capable of having an anionic charge and a cationic charge at a pH of from about 4 to about 12;

vi) units having no charge at a pH of from about 4 to about 12; and

vii) mixtures of units (iv), (v), (vi), and (vii).

The following describe non-limiting examples of polymeric material which may be suitable for use in the liquid detergent compositions of the present invention.

Polymeric Suds Stabilizers (Suds Boosters)

The polymeric suds stabilizers of the present invention are polymers which contain units capable of having a cationic charge at a pH of from about 4 to about 12, provided that the suds stabilizer has an average cationic charge density of 2.77 or less, preferably 2.75 or less, more preferably from about 0.01 to about 2.75, more preferably

0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12.

Preferably, the polymeric suds stabilizers also include units capable of influencing the average cationic charge density of the polymeric suds stabilizers, preferably by decreasing the average cationic charge density of the polymeric suds stabilizers. Such units capable of influencing the average cationic charge density of the polymeric suds stabilizers may, and preferably do, provide additional advantageous properties to the polymeric suds stabilizers that increase their cleaning and/or suds boosting and/or suds retention properties. Further, such units may increase the interactions between the polymer, which is neutral or positively charged, and the soil which is negatively charged.

Additionally, the polymeric suds stabilizer can be present as the free base or as a salt. Typical counter ions include, acetate, citrate, maleate, sulfate, chloride, etc.

Further, the polymeric suds stabilizers of the present invention may be copolymers, terpolymers with random and/or repeating units, and/or block polymers such as di-, tri- and multi-block polymers.

For example a copolymer can be made from two monomers, G and H, such that G and H are randomly distributed in the copolymer, such as

GHGGHGGGGGHHG.....etc.

or G and H can be in repeating distributions in the copolymer, for example

GHGHGHGHGHGHGH .....etc.,

or

GGGGGHHGGGGGHH.....etc.,

The same is true of the terpolymer, the distribution of the three monomers can be either random or repeating.

A particular process may be advantageous to make copolymers from at least one tertiary amino-containing monomer, e.g., dimethylaminoethyl(meth)acrylate, and at least one vinyl-containing monomer, when the at least one vinyl-functional monomer is not substituted by an alkyl group on the 2-position of the vinyl moiety (for example, not methacrylic acid, hydroxyethylmethacrylate or hydroxypropylmethacrylate). This is advantageous to make such copolymers free of or having minimal Michael addition adducts of the ingredients. Also, Michael addition adducts form but revert back to monomers if the hydrogen atom is substituted by an alkyl group on the 2-position of the vinyl moiety.

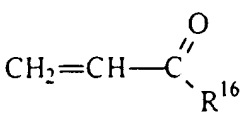
In the process, at least one tertiary amino-containing monomer, at least one vinyl-containing monomer not substituted by an alkyl group on the 2-position of the vinyl moiety, an acid, and a polymerization initiator are mixed in a polymerization reactor to form a polymerization mixture in the reactor. The at least one tertiary amino-containing monomer and the at least one vinyl-containing monomer are copolymerized in the polymerization mixture, to form a copolymer, and optionally a Michael addition adduct of the at least one tertiary amino-containing monomer and the at least one vinyl-containing monomer. However, Michael adduct formation is prevented/minimized by performing at least one of the following steps in a process for making copolymers from tertiary amino monomers and vinyl-functional monomers:

1. Avoid formation of adduct by separating the tertiary amino monomer (e.g. dimethylaminoethyl(meth)acrylate) from the vinyl-functional monomer prior to polymerization.

2. Avoid formation of adduct by maintaining the at least one tertiary amino-containing monomer and the at least one vinyl-functional monomer water-free prior to the copolymerizing.

3. Conduct polymerization at a high temperature (typically about 70 to about 90°C, preferably about 80 to about 90°C) and at a suitable pH (typically about 3 to about 10, preferably about 4 to about 8, most preferably about 4 to about 6) to cause the adduct formed to be unstable and revert to monomers. Thus, monomers bound by the adduct will be liberated to copolymerize.

Typically, the at least one vinyl-functional monomer has is selected from at least one member of the group consisting of a monomer of Formula VIIa:



VIIa

wherein R^{16} is a group which permits the vinyl-functional monomer to undergo Michael addition.

Preferably, the acid reactants, e.g., mineral acid (for example sulfuric acid) or citric acid, is fed to the reactor before the monomers. Typically these processes are performed as semi-batch processes. However, batch or continuous processes are not precluded.

In a particular embodiment, a tertiary amino-containing monomer, water, and an acid may be mixed in a reactor to form a neutralized tertiary amino-containing monomer mixture having a pH of about 3 to about 10. The neutralized tertiary amino-containing monomer mixture, a vinyl-functional monomer, water, and an initiator are fed to the reactor. The initiator may be a single ingredient (typically sodium persulfate) or a redox system combining an oxidizing component (typically sodium persulfate) and a reducing component (typically sodium metabisulfite). Water is typically fed directly to the reactor with the vinyl-functional monomer and neutralized tertiary amino-containing monomer, and/or with other ingredients.

Generally, the neutralized tertiary amino-containing monomer mixture, a vinyl-functional monomer/water mixture, and initiator are separately fed to the reactor. Preferably, the neutralized tertiary amino-containing monomer mixture, the vinyl-functional monomer/water mixture, at least a portion of the initiator are separately, yet simultaneously, fed to the reactor to form the polymerization mixture. The initiator can be a single organic or inorganic compound or a redox (reduction/oxidation) system of two or more compounds. For example, United States patent no. 5,863,526, incorporated herein by reference in its entirety, discloses typical initiator systems. The polymerization mixture is maintained in the reactor at polymerization conditions including a pH of about 3 to about 10, preferably about 4 to about 8, most preferably about 4 to about 6, and a temperature of about 70 to about 90°C, preferably about 80 to about 90°C, for a time of about 1 to about 3 hours, to form a copolymer and the copolymer product is recovered.

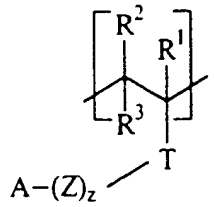
In a second embodiment, water and acid are fed first to the reactor. Then, water-free tertiary amino-containing monomer, water-free vinyl-functional monomer and initiator are separately fed to the reactor to admix with the acid and water in the reactor. In the reactor, the monomers polymerize in the presence of the initiator described above.

Generally, the water is provided with acid and initiator. The polymerization mixture is maintained at the above-described polymerization conditions to form the copolymer product. Then the copolymer product is recovered. If desired, the tertiary amino-containing monomer, the vinyl-functional monomer, and the initiator are separately, yet simultaneously fed to the reactor.

In a third embodiment the process may be the same as the second embodiment except that the water-free monomers are mixed to form a water-free mixture prior to being fed to the reactor.

Cationic Units

For the purposes of the present invention the term "cationic unit" is defined as "a moiety which when incorporated into the structure of the suds stabilizers of the present invention, is capable of maintaining a cationic charge within the pH range of from about 4 to about 12. The cationic unit is not required to be protonated at every pH value within the range of about 4 to about 12." Non-limiting examples of units which comprise a cationic moiety include the cationic units having the formula:



[I]

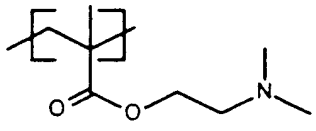
wherein each of R^1, R^2 and R^3 are independently selected from the group consisting of hydrogen, C_1 to C_6 alkyl, and mixtures thereof, preferably hydrogen, C_1 to C_3 alkyl, more preferably, hydrogen or methyl. T is selected from the group consisting of substituted or unsubstituted, saturated or unsaturated, linear or branched radicals selected from the group consisting of alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, ester, ether, carbonyl, amido, amino, glycidyl, carbanato, carbamate, carboxylic, and carboalkoxy radicals and mixtures thereof. Z is selected from the group consisting of: $-(CH_2)-$, $(CH_2-CH=CH)-$, $-(CH_2-CHOH)-$, $(CH_2-CHNR^4)-$, $-(CH_2-CHR^5-O)-$ and mixtures thereof, preferably $-(CH_2)-$. R^4 and R^5 are selected from the group consisting of hydrogen, C_1 to C_6 alkyl and mixtures thereof, preferably hydrogen, methyl, ethyl and mixtures thereof; z is an integer selected from about 0 to about 12, preferably about 2 to about 10, more preferably about 2 to about 6. A

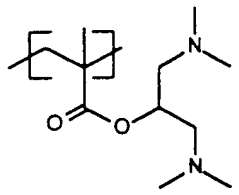
is NR^6R^7 or $NR^6R^7R^8$. Wherein each of R^6, R^7 and R^8, when present, are independently selected from the group consisting of H, C_1-C_8 linear or branched alkyl, alkyleneoxy having the formula:

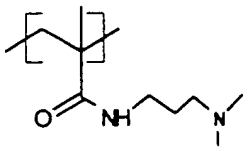
$$—(R^9O)_yR^{10}$$

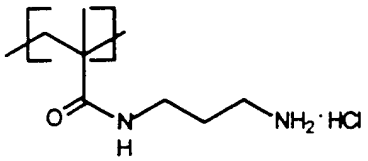
wherein R^9 is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^{10} is hydrogen, C_1-C_4 alkyl, and mixtures thereof: y is from 1 to about 10. Preferably R^6, R^7 and R^8, when present, are independently, hydrogen, C_1 to C_4 alkyl. Alternatively, NR^6R^7 or $NR^6R^7R^8$ can form a heterocyclic ring containing from 4 to 7 carbon atoms, optionally containing additional hetero atoms, optionally fused to a benzene ring, and optionally substituted by C_1 to C_8 hydrocarbyl, and/or acetates. Examples of suitable heterocycles, both substituted and unsubstituted, are indolyl, isoindolinyl imidazolyl, imidazolinyl, piperidinyl pyrazolyl, pyrazolinyl, pyridinyl, piperazinyl, pyrrolidinyl, pyrrolidinyl, guanidino, amidino, quinidinyl, thiazolinyl, morpholine and mixtures thereof, with morpholino and piperazinyl being preferred. Furthermore the polymeric suds stabilizer has a molecular weight of from about 1,000 to about 2,000,000 preferably from about 5,000 to about 1,000,000, more preferably from about 10,000 to about 750,000, more preferably from about 20,000 to about 500,000, even more preferably from about 35,000 to about 300,000 daltons. The molecular weight of the polymeric suds boosters, can be determined via conventional gel permeation chromatography or any other suitable procedure known to those of ordinary skill in the art.

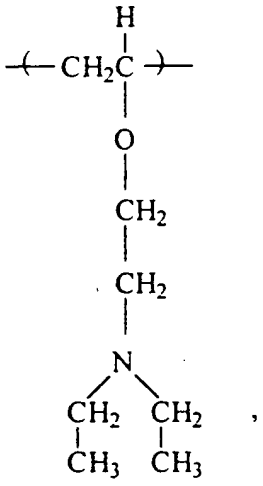
Examples of the cationic unit of formula [I] include, but are not limited to, the following structures:

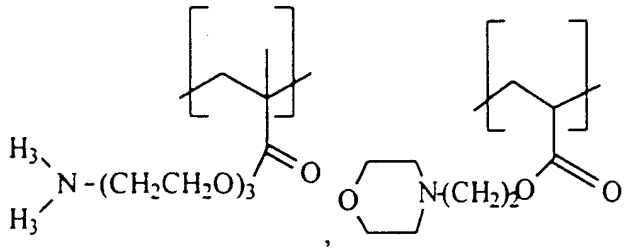


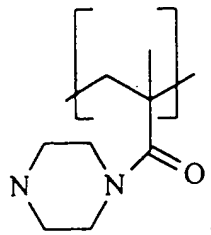




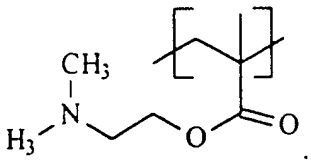








A preferred cationic unit is 2-dimethylaminoethyl methacrylate (DMAM) having the formula:



Hydroxyl-Containing Units

The hydroxyl group density of a polymeric suds stabilizer of the present invention is determined by the following calculation.

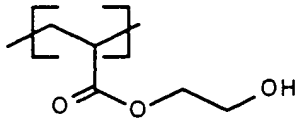
$$\text{Hydroxyl Group Density} = \frac{[\text{Molecular Weight of Hydroxyl Group}]}{[\text{Total Monomer Molecular Weight}]}$$

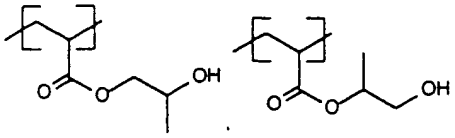
For example, the Hydroxyl Group Density of a polymeric suds stabilizer containing 2-dimethylaminoethyl methacrylate having a molecular weight of approximately 157 and hydroxyethylacrylate having a molecular weight of approximately 116 grams/mole, at a 1:3 mole ratio would be calculated as follows:

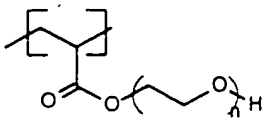
$$\text{Hydroxyl Group Density} = \frac{[17]}{[3(116) + 157]} = 0.0337$$

Preferably, the polymeric suds stabilizers of the present invention have a Hydroxyl Group Density of about 0.5 or less, preferably from about 0.0001 to about 0.4.

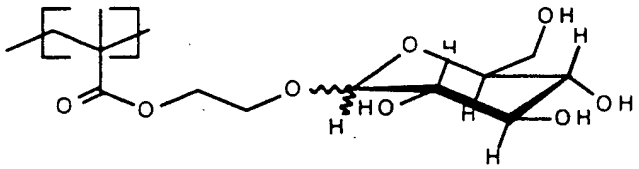
Nonlimiting examples of such hydroxyl group-containing units include, but are not limited to the following:

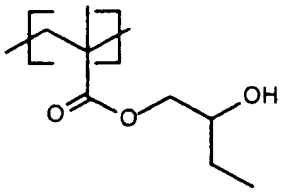


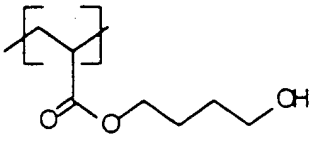


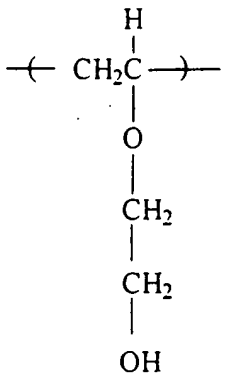


wherein n is an integer from 2 to 100, preferably 2 to 50, more preferably 2 to 30,





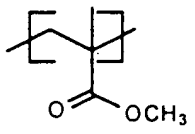


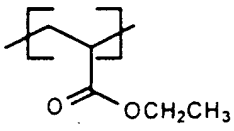


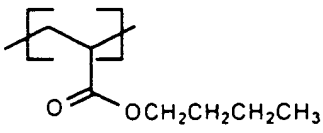
Hydrophobic Units

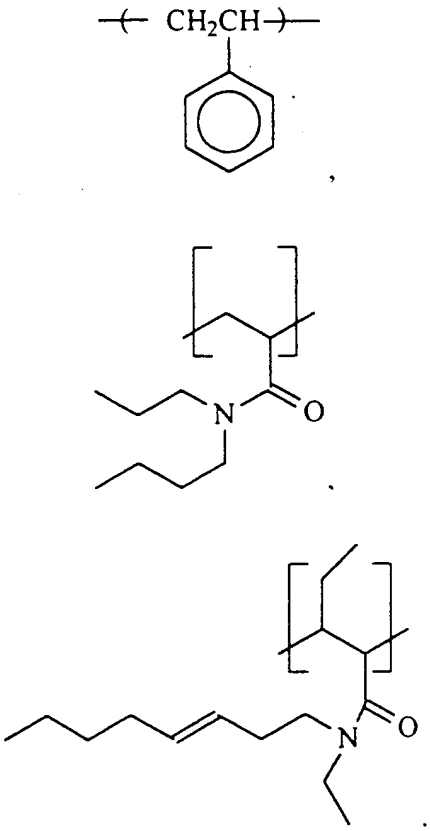
Suitable hydrophobic group-containing units for use in the present invention include, but are not limited to, hydrophobic groups preferably selected from the group consisting of non-hydroxyl groups, non-cationic groups, non-anionic groups, non-carbonyl groups, and/or non-H-bonding groups, more preferably selected from the group consisting of alkyls, cycloalkyls, aryls, alkaryls, aralkyls and mixtures thereof.

Nonlimiting examples of such hydrophobic group-containing units include, but are not limited to the following:





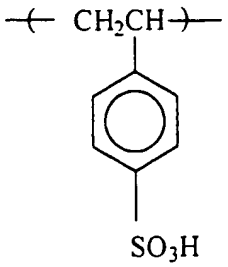


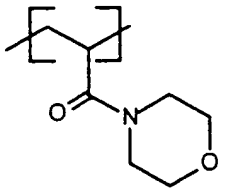


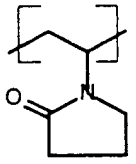
Hydrophilic Units

Suitable hydrophilic group-containing units for use in the present invention include, but are not limited to, hydrophilic groups preferably selected from the group consisting of carboxyl groups, carboxylic acids and their salts, sulfonic acids and their salts, heteroatom-containing moieties present in a ring or linear form and mixtures thereof.

Nonlimiting examples of such hydrophilic group-containing units include, but are not limited to the following:

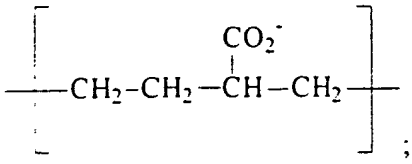




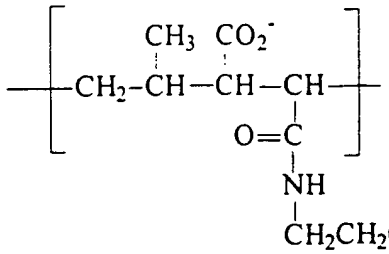


Anionic Units

For the purposes of the present invention the term "anionic unit" is defined as "a moiety which when incorporated into the structure of the suds stabilizers of the present invention, is capable of maintaining an anionic charge within the pH range of from about 4 to about 12. The anionic unit is not required to be de-protonated at every pH value within the range of about 4 to about 12." Non-limiting examples of units which comprise a anionic moiety include, acrylic acid, methacrylic acid, glutamic acid, aspartic acid, the monomeric unit having the formula:



and the monomeric unit having the formula:



the latter of which also comprises a moiety capable of having a cationic charge at a pH of about 4 to about 12. This latter unit is defined herein as "a unit capable of having an anionic and a cationic charge at a pH of from about 4 to about 12."

Non-charged Units

For the purposes of the present invention the term "non-charged unit" is defined as "a moiety which when incorporated into the structure of the suds stabilizers of the present invention, has no charge within the pH range of from about 4 to about 12." Non-limiting examples of units which are "non-charged units" are styrene, ethylene, propylene, butylene, 1,2-phenylene, esters, amides, ketones, ethers, and the like.

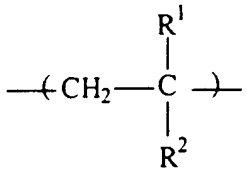
The units which comprise the polymers of the present invention may, as single units or monomers, have any pK_a value.

Preferably, the polymeric suds stabilizers are selected from copolymers, which can optionally be crosslinked, terpolymers and other polymers (or multimers).

Particular Polymers

Preferred polymers of the present invention comprise:

A. at least one cationic monomeric unit A having a Formula I:

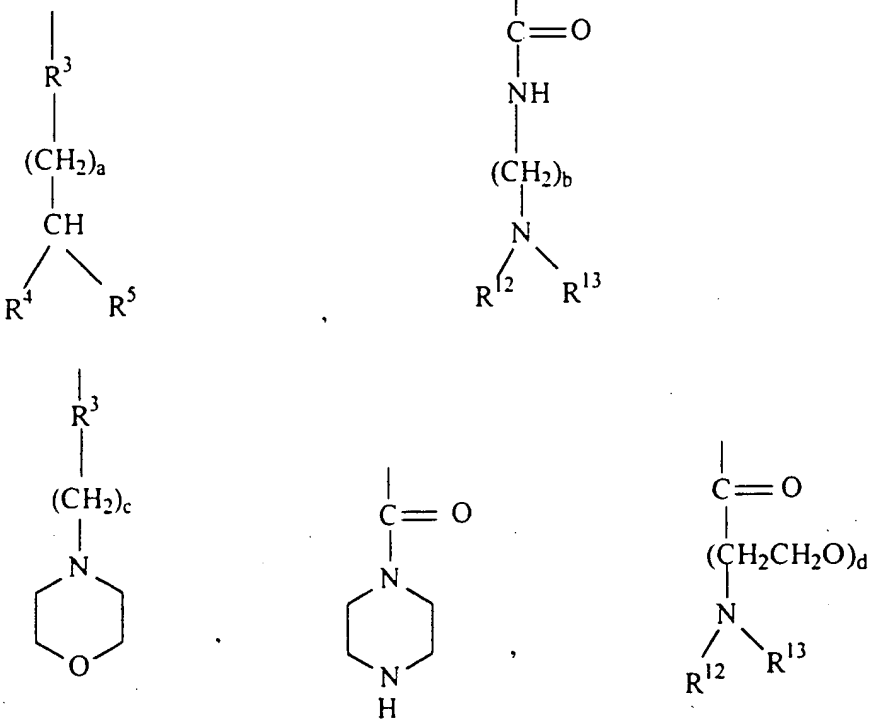


I

wherein

R^1 is H or an alkyl having 1 to 10 carbon atoms,

R^2 is a moiety selected from the group consisting of



wherein R^3 is selected from the group consisting of

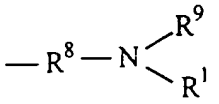
a is an integer from 0 to 16, preferably 0 to 10;

b is an integer from 2 to 10;

c is an integer from 2 to 10;

d is an integer from 1 to 100;

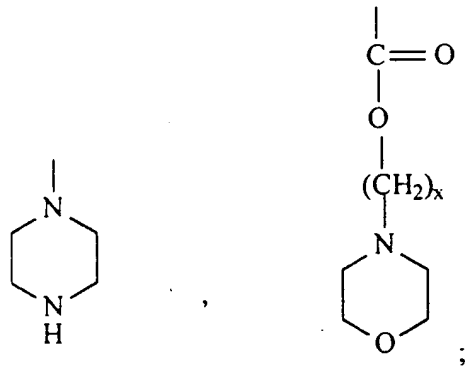
R^4 and R^5 are independently selected from the group consisting of -H, and



R^8 is independently selected from the group consisting of a bond or an alkylene having 1 to 18 carbon atoms;

R^9 and R^{10} are independently selected from the group consisting of -H, alkyl having 1 to 8 carbon atoms, and an olefin chain having 2 to 8 carbon atoms;

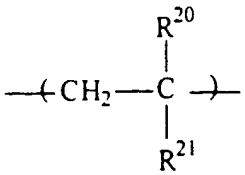
R^{12} and R^{13} are independently selected from the group consisting of H and alkyl having from 1 to 8 carbon atoms;



wherein x is an integer from 2 to 10;

B. at least one monomeric unit B selected from the group consisting of:

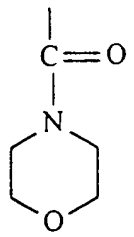
a monomeric unit of Formula IV



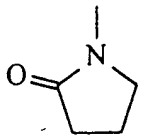
VI

wherein R^{20} is selected from the group consisting of H and CH_3;

R^{21} is selected from the group consisting of:



,



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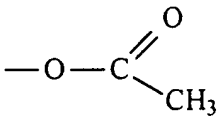
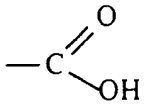


,

—OH ,



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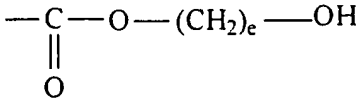
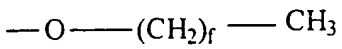
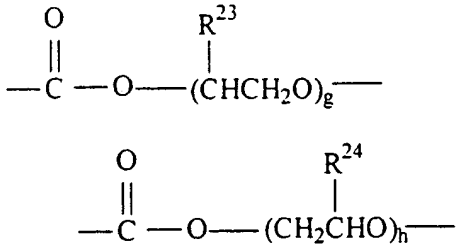


;

wherein e is an integer from 3 to 25, preferably from 3 to 5;



wherein f is an integer from 0 to 25, preferably from 0 to 12;



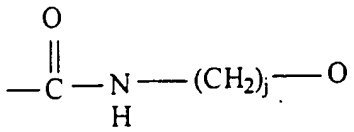
;

wherein g is an integer from 1 to 100, preferably 1 to 50;

wherein h is an integer from 1 to 100, preferably 1 to 50;

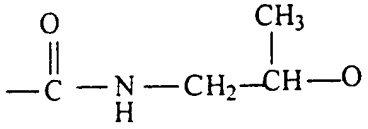
R^{23} is -H, $-CH_3$ or $-C_2H_5$;

R^{24} is $-CH_3$ or $-C_2H_5$;



;

wherein j is an integer from 1 to 25, preferably 2 to 12;



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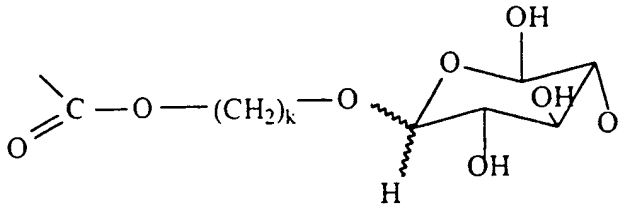
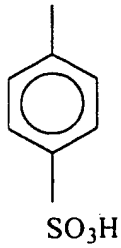


;

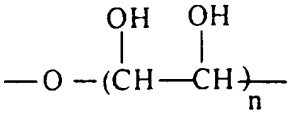
wherein k is an integer from 1 to 25, preferably 1 to 12;



,

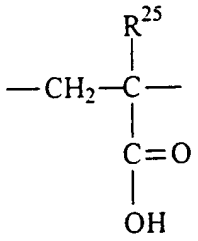
-NH-$(CH_2)_m$-NH_2·HCl, wherein m is an integer from 1 to 25, preferably 2 to 12; and

a polyhydroxy monomeric unit of Formula VI:

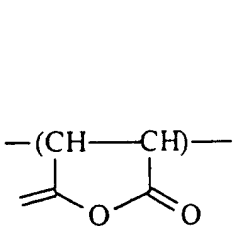


wherein n is an integer from 1 to 50, preferably 1 to 25; and

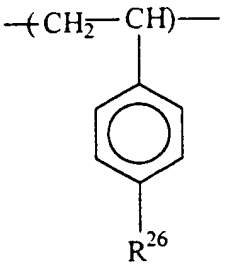
C. optionally at least one monomeric unit C selected from the group consisting of:



wherein R^{25} is -H or $-CH_3$;



and

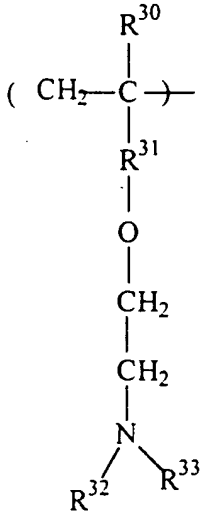


;

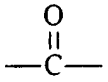
wherein R^{26} is -H.

A preferred terpolymer and/or multimer of the present invention comprises at least one said monomeric unit A, at least one said monomeric unit B and at least one said monomeric unit C.

Preferably, at least one monomeric unit A is selected from the group consisting of:



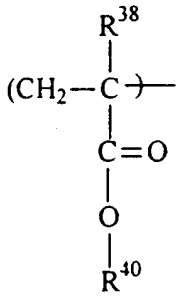
wherein R^{30} is H or $-CH_3$,

wherein R^{31} is a bond or  , and

R^{32} and R^{33} are $-CH_3$ or $-C_2H_5$.

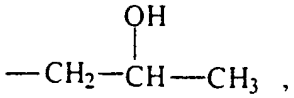
Preferably, the polymer is a terpolymer in which:

said at least one monomeric unit B is selected from the group consisting of:



wherein R^{38} is selected from the group consisting of H and CH_3 and

R^{40} is selected from the group consisting of $-CH_2CH_2$-OH and

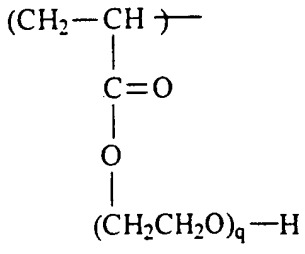
 ,

and isomers thereof;

said terpolymer comprising said at least one monomeric unit C,

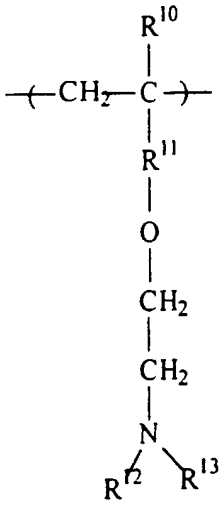
wherein the molar ratio of said monomeric unit A : monomeric unit B : monomeric unit C is 1 to 9 : 1 to 9 : 1 to 6 respectively.

Preferably, the polymer has at least one monomeric unit B which has the formula:

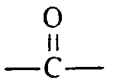


wherein q ranges from 1 to 12, preferably 1 to 10, more preferably 1 to 9.

Preferably, the polymer is a terpolymer, in which at least one monomeric unit A is selected from the group consisting of:

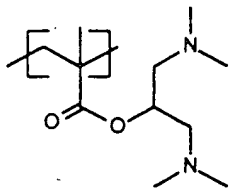


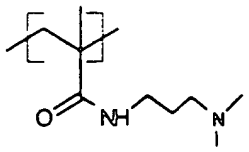
wherein R^{10} is H or CH_3,

R^{11} is a bond or  , and R^{12} and R^{13} are $-CH_3$ or $-C_2H_5$, and said polymer comprises said at least one monomeric unit C.

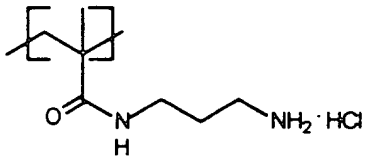
Preferably, the molar ratio of monomeric unit A : monomeric unit B : monomeric unit C ranges from 1 to 9 : 1 to 9 : 1 to 3 respectively.

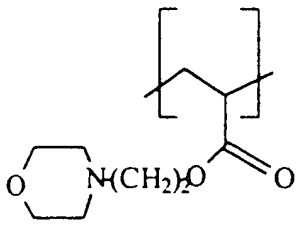
Preferably, at least one monomeric unit A has a formula selected from the group consisting of:

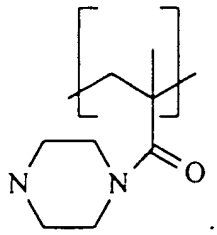




Preferably, at least one monomeric unit A has a formula selected from the group consisting of:

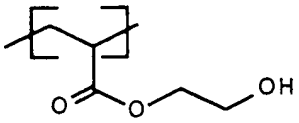


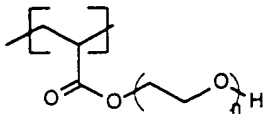




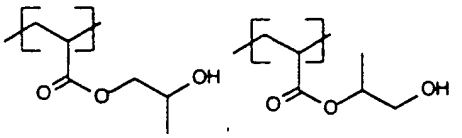
Preferably, at least one one monomeric unit B is selected from the group

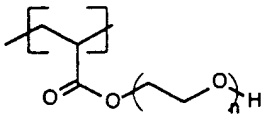
consisting of:

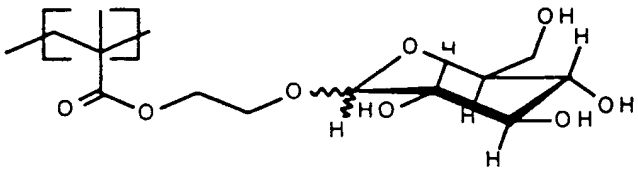


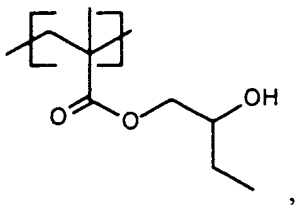


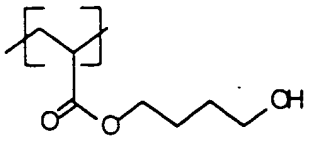
wherein n is an integer from 2 to 50, preferably 2 to 30, more preferably 2 to 27;











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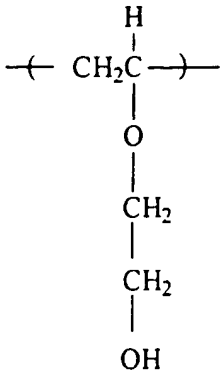

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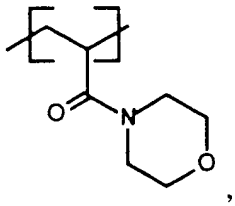

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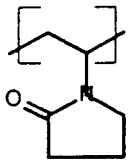

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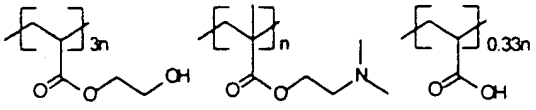
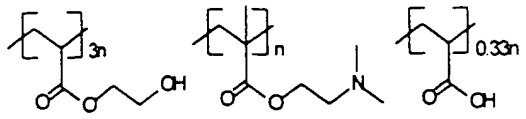
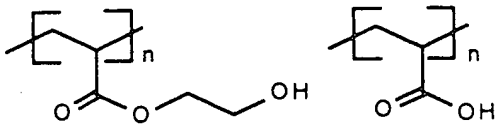
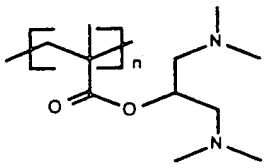
Specific Polymers

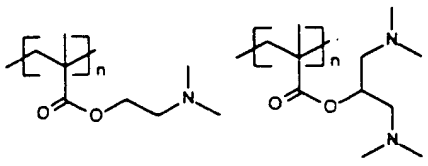
Nonlimiting examples of such copolymers, which can optionally be crosslinked, terpolymers and multimers have the following formulas:

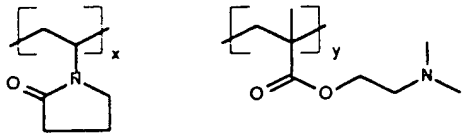




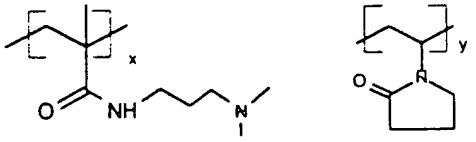








x=3, y=7



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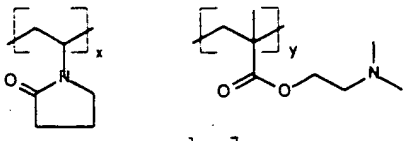
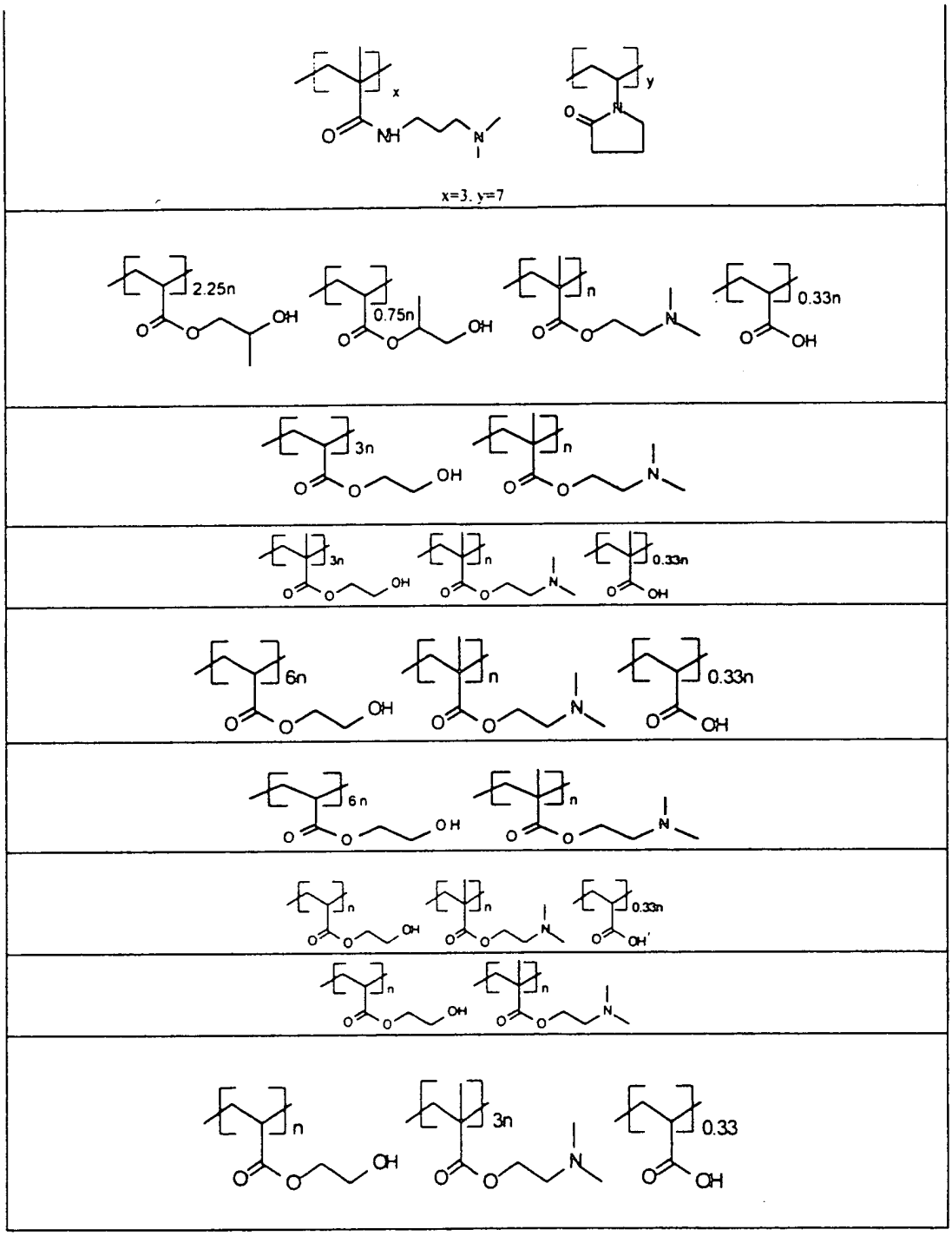
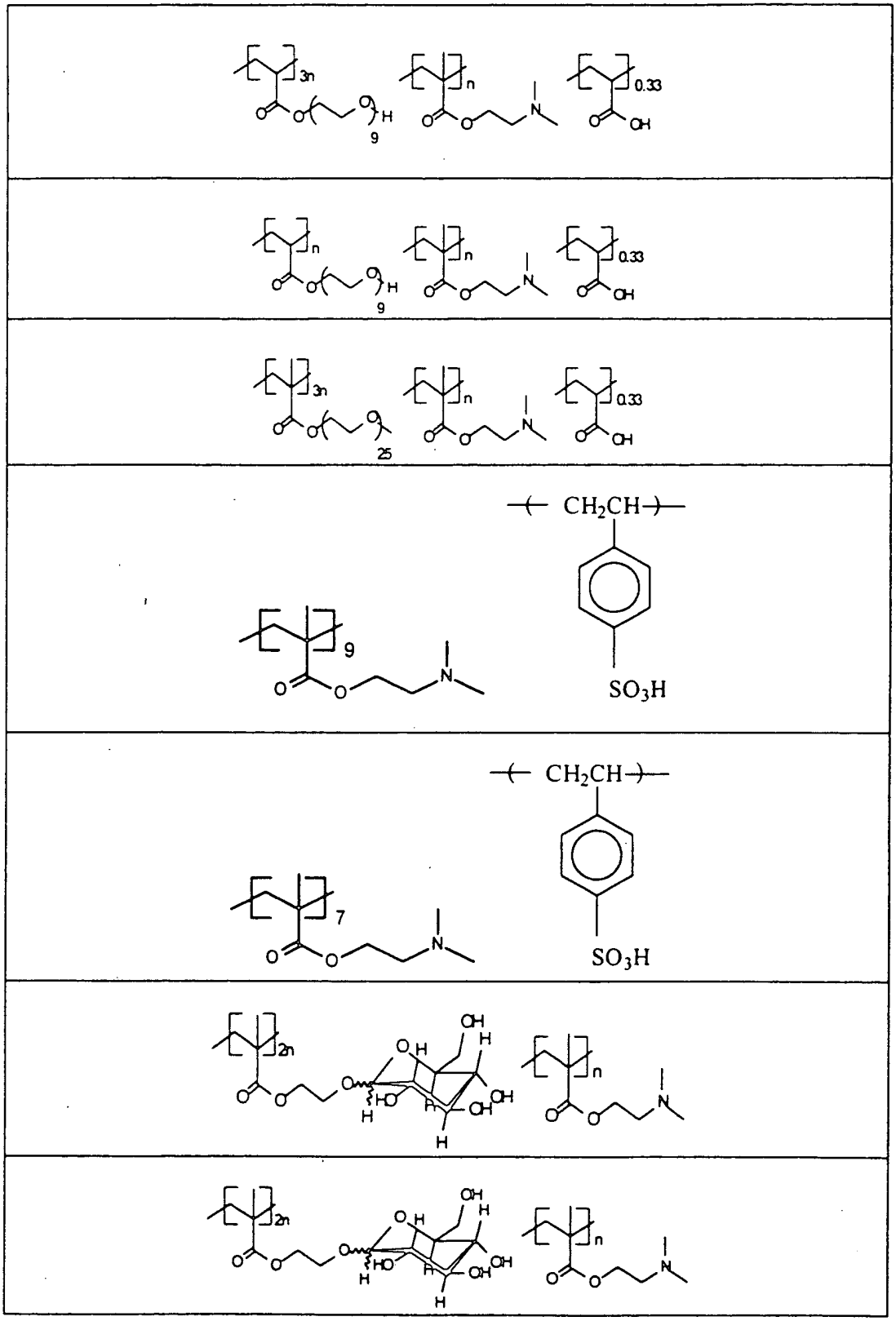
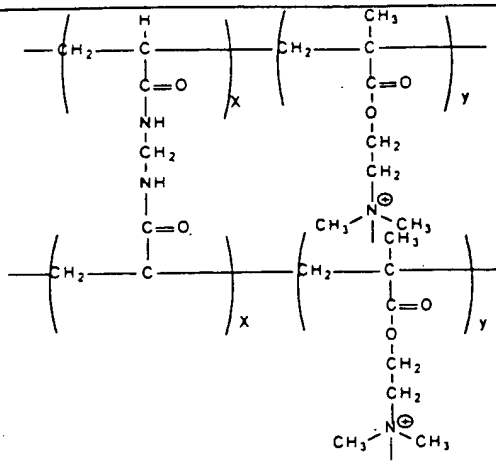


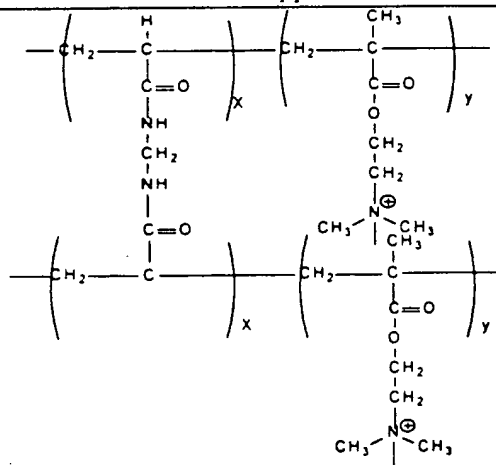
x=3, y=7


x=3. y=7

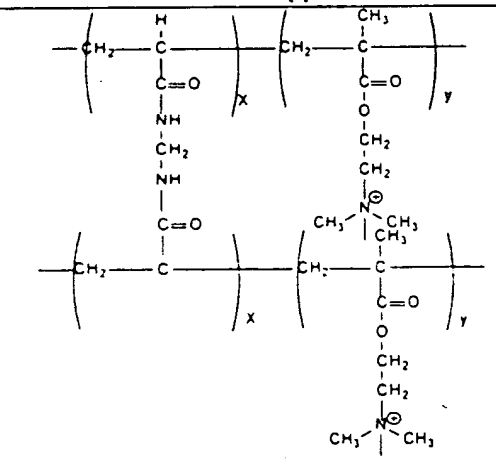




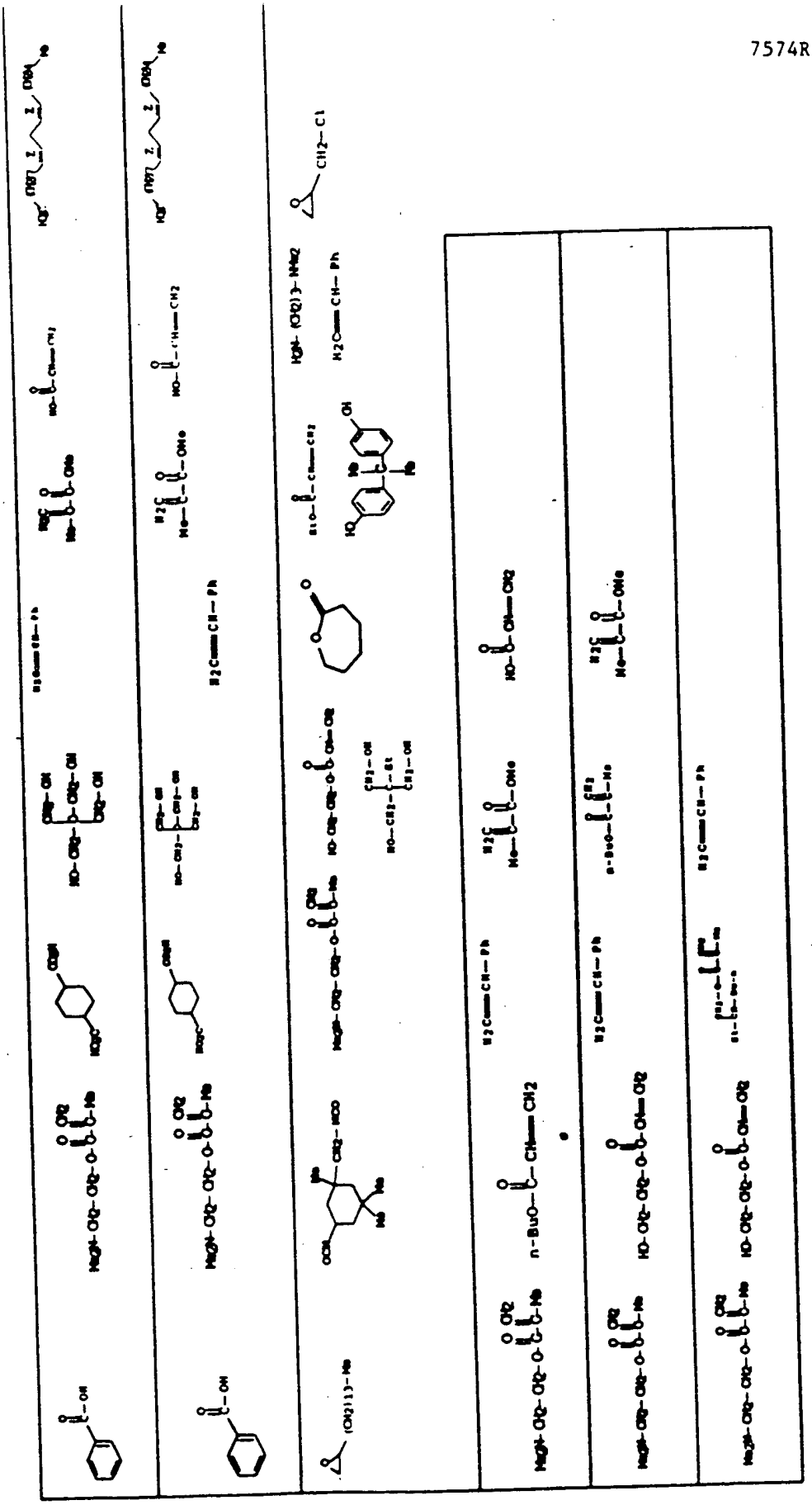
x = 50 ppm

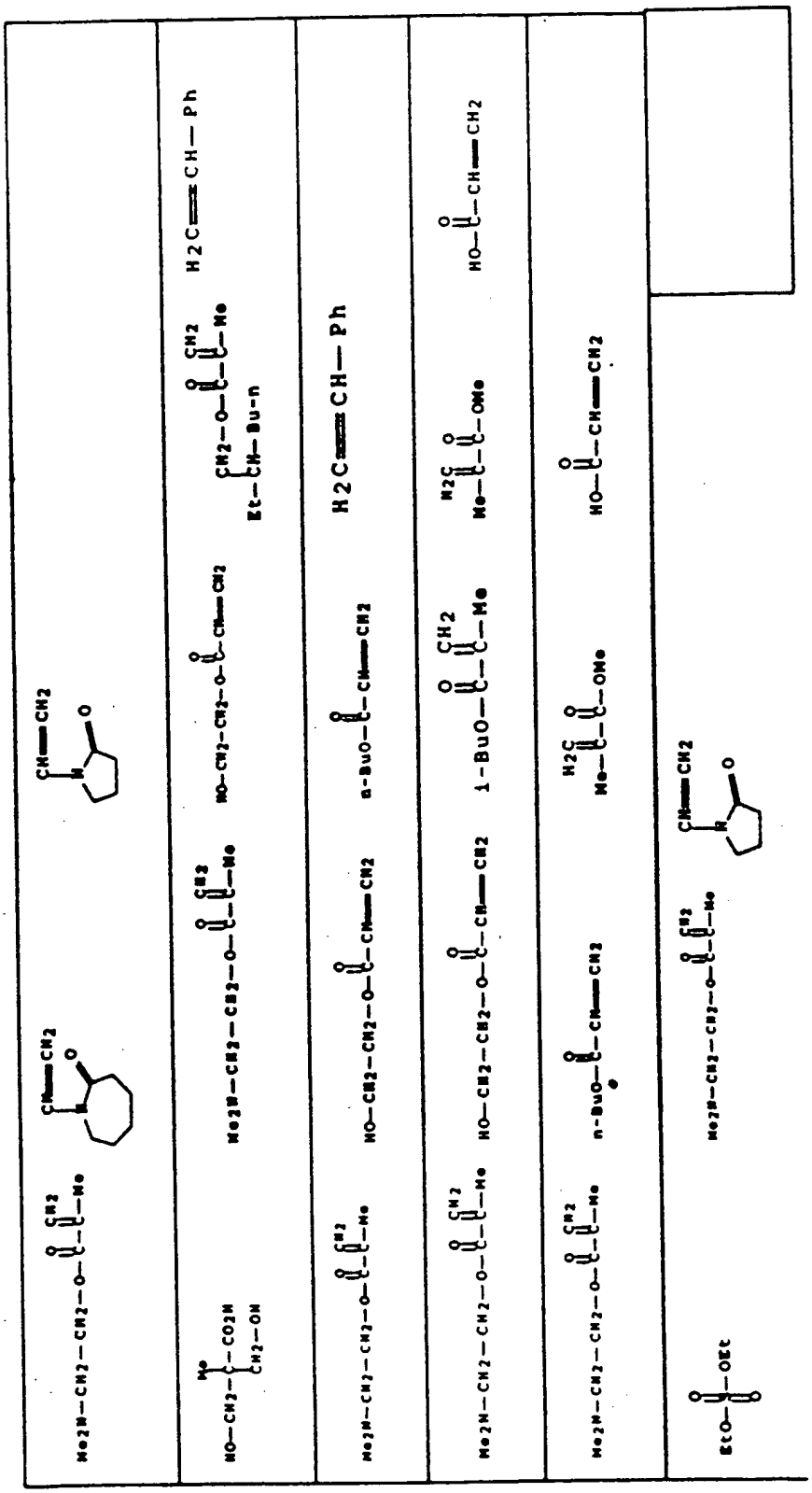


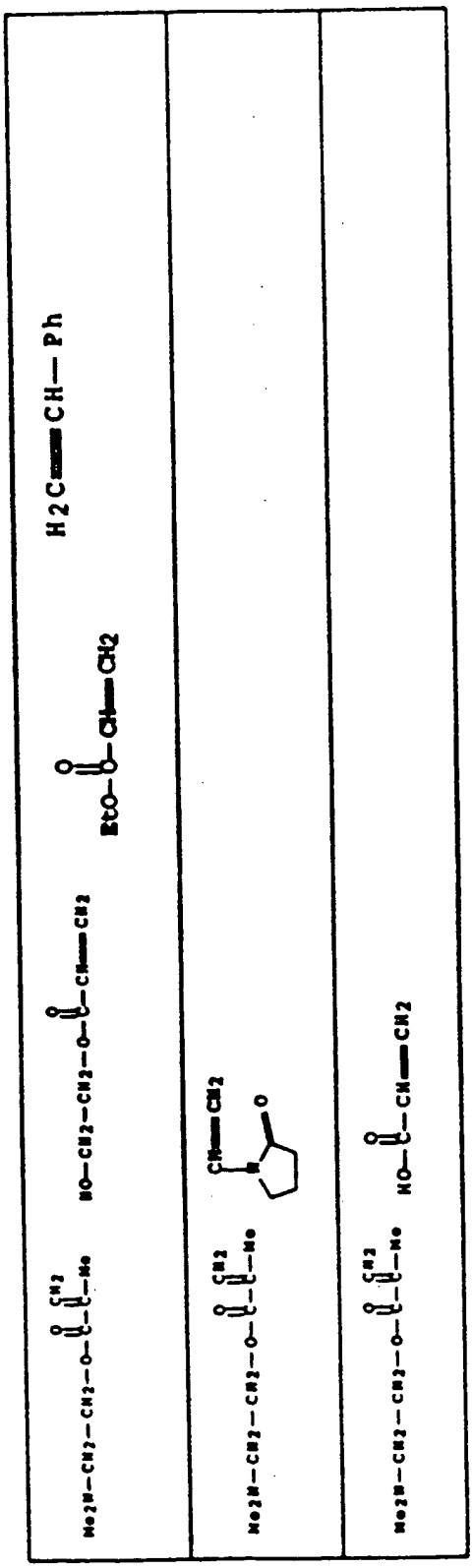
x = 200 ppm



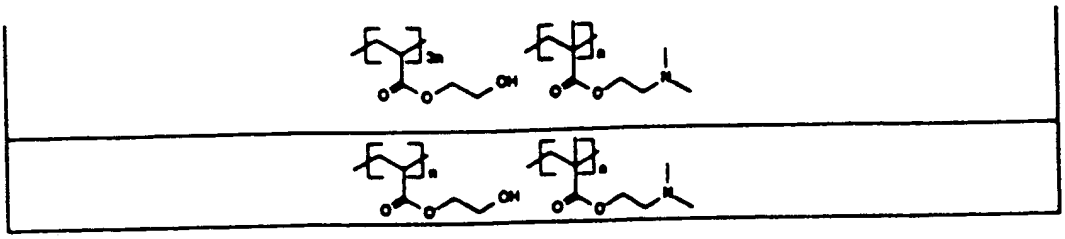
x = 1000 ppm



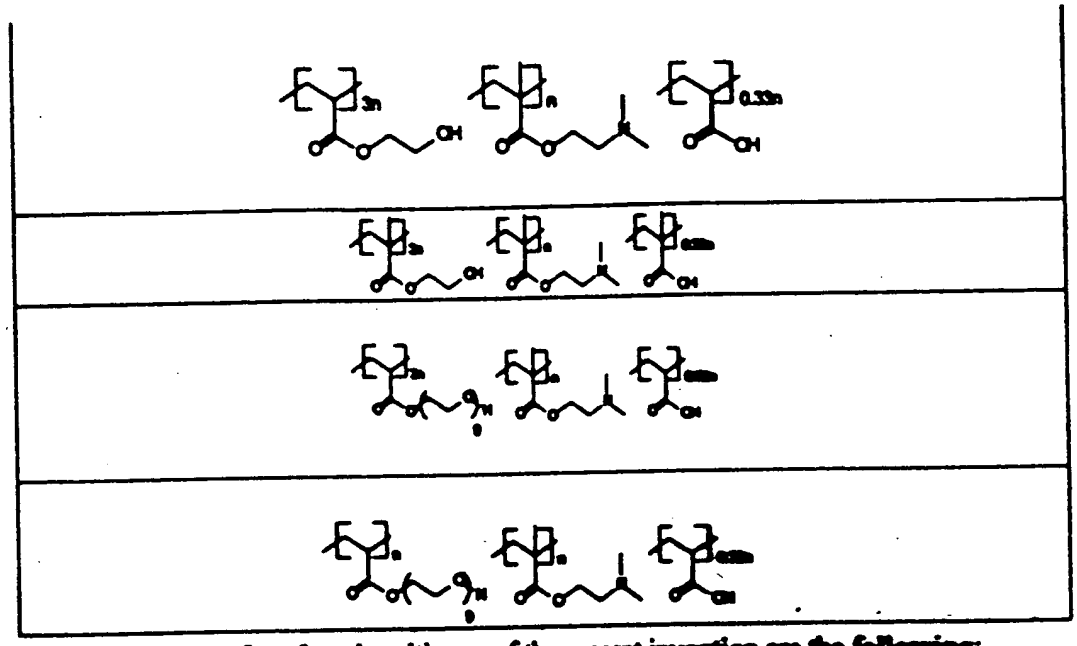




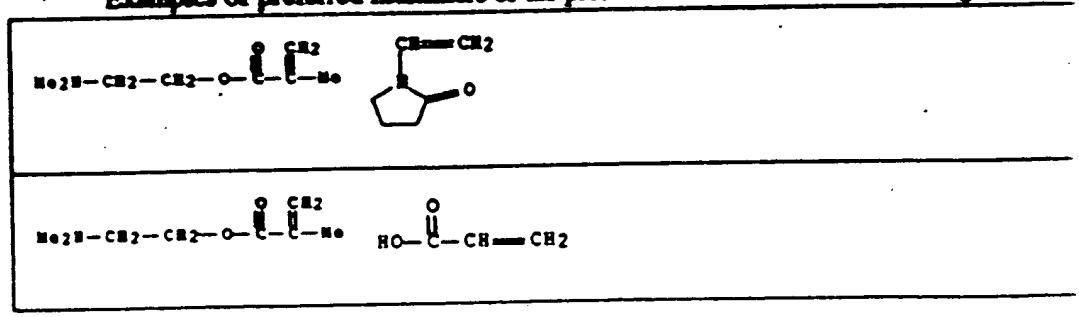
Examples of preferred copolymers of the present invention are the following:

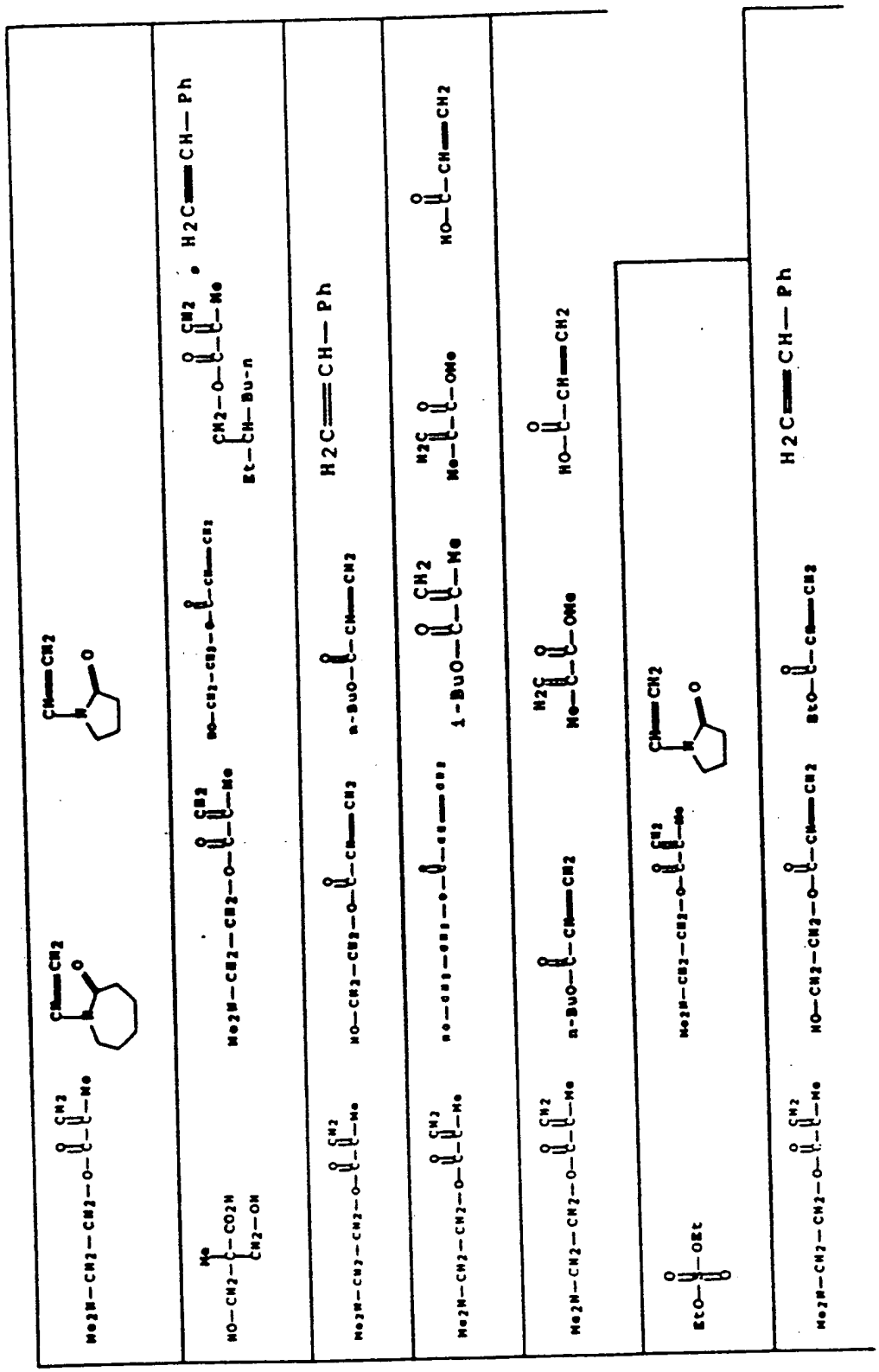


Examples of preferred terpolymers of the present invention are the following:



Examples of preferred multimers of the present invention are the following:





The liquid detergent compositions according to the present invention comprise at least an effective amount of the polymeric suds stabilizers described herein, preferably from about 0.01% to about 10%, more preferably from about 0.001% to about 5%, most preferably from about 0.1% to about 2% by weight, of said composition. What is meant herein by "an effective amount polymeric suds stabilizers " is that the suds volume and suds duration produced by the presently described compositions are sustained for an increased amount of time relative to a composition which does not comprise one or more of the polymeric suds stabilizer described herein. Additionally, the polymeric suds stabilizer can be present as the free base or as a salt. Typical counter ions include, acetate, citrate, maleate, sulfate, chloride, etc.

Proteinaceous Suds Stabilizers

The proteinaceous suds stabilizers of the present invention can be peptides, polypeptides, amino acid containing copolymers, terpolymers etc., and mixtures thereof. Any suitable amino acid can be used to form the backbone of the peptides, polypeptides, or amino acid, wherein the polymers have an average cationic charge density of 2.77 or less, preferably of 2.75 or less, more preferably from about 0.01 to about 2.75, even more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12.

In general, the amino acids suitable for use in forming the proteinaceous suds stabilizers of the present invention have the formula:

$$H_2N-(C)_x-\underset{R^2}{\overset{R}{C}}-(C)_y-\underset{R^2}{\overset{R^2}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

wherein R and R^1 are each independently hydrogen, C_1-C_6 linear or branched alkyl, C_1-C_6 substituted alkyl, and mixtures thereof. Non-limiting examples of suitable moieties for substitution on the C_1-C_6 alkyl units include amino, hydroxy, carboxy, amido, thio, thioalkyl, phenyl, substituted phenyl, wherein said phenyl substitution is hydroxy, halogen, amino, carboxy, amido, and mixtures thereof. Further non-limiting examples of suitable moieties for substitution on the R and R^1 C_1-C_6 alkyl units include 3-imidazolyl, 4-imidazolyl, 2-imidazolinyl, 4-imidazolinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1-pyrazolyl, 3-pyrazoyl, 4-pyrazoyl, 5-pyrazoyl, 1-pyrazolinyl, 3-pyrazolinyl, 4-pyrazolinyl, 5-pyrazolinyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, piperazinyl, 2-pyrrolidinyl, 3-pyrrolidinyl, guanidino, amidino, and mixtures thereof. Preferably R^1 is hydrogen and at least 10% of R units are moieties which are capable of having a

The liquid detergent compositions according to the present invention comprise at least an effective amount of the polymeric suds stabilizers described herein, preferably from about 0.01% to about 10%, more preferably from about 0.001% to about 5%, most preferably from about 0.1% to about 2% by weight, of said composition. What is meant herein by "an effective amount polymeric suds stabilizers " is that the suds volume and suds duration produced by the presently described compositions are sustained for an increased amount of time relative to a composition which does not comprise one or more of the polymeric suds stabilizer described herein. Additionally, the polymeric suds stabilizer can be present as the free base or as a salt. Typical counter ions include, acetate, citrate, maleate, sulfate, chloride, etc.

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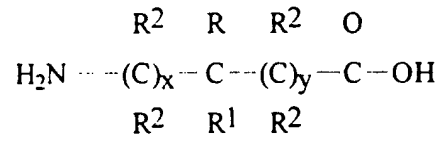
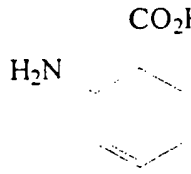
In general, the amino acids suitable for use in forming the proteinaceous suds stabilizers of the present invention have the formula:



wherein R and R^1 are each independently hydrogen, C_1-C_6 linear or branched alkyl, C_1-C_6 substituted alkyl, and mixtures thereof. Non-limiting examples of suitable moieties for substitution on the C_1-C_6 alkyl units include amino, hydroxy, carboxy, amido, thio, thioalkyl, phenyl, substituted phenyl, wherein said phenyl substitution is hydroxy, halogen, amino, carboxy, amido, and mixtures thereof. Further non-limiting examples of suitable moieties for substitution on the R and R^1 C_1-C_6 alkyl units include 3-imidazolyl, 4-imidazolyl, 2-imidazolinyl, 4-imidazolinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1-pyrazolyl, 3-pyrazoyl, 4-pyrazoyl, 5-pyrazoyl, 1-pyrazolinyl, 3-pyrazolinyl, 4-pyrazolinyl, 5-pyrazolinyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, piperazinyl, 2-pyrrolidinyl, 3-pyrrolidinyl, guanidino, amidino, and mixtures thereof. Preferably R^1 is hydrogen and at least 10% of R units are moieties which are capable of having a positive or negative charge at a pH of from about 4 to about 12. Each R^2 is independently hydrogen, hydroxy, amino, guanidino, C_1-C_4 alkyl, or comprises a carbon chain which can be

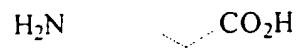
taken together with R, R^1 any R^2 units to form an aromatic or non-aromatic ring having from 5 to 10 carbon atoms wherein said ring may be a single ring or two fused rings, each ring being aromatic, non-aromatic, or mixtures thereof. When the amino acids according to the present invention comprise one or more rings incorporated into the amino acid backbone, then R, R^1, and one or more R^2 units will provide the necessary carbon-carbon bonds to accommodate the formation of said ring. Preferably when R is hydrogen, R^1 is not hydrogen, and vice versa; preferably at least one R^2 is hydrogen. The indices x and y are each independently from 0 to 2.

An example of an amino acid according to the present invention which contains a ring as part of the amino acid backbone is 2-aminobenzoic acid (anthranilic acid) having the formula:



wherein x is equal to 1, y is equal to 0 and R, R^1, and 2 R^2 units from the same carbon atom are taken together to form a benzene ring.

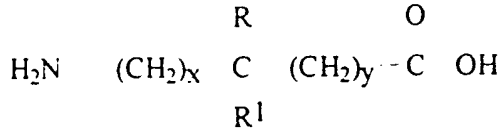
A further example of an amino acid according to the present invention which contains a ring as part of the amino acid backbone is 3-aminobenzoic acid having the formula:



wherein x and y are each equal to 1, R is hydrogen and R^1 and four R^2 units are taken together to form a benzene ring.

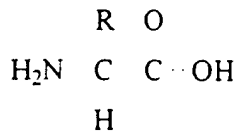
Non-limiting examples of amino acids suitable for use in the proteinaceous suds stabilizers of the present invention wherein at least one x or y is not equal to 0 include 2-aminobenzoic acid, 3-aminobenzoic acid, 4-aminobenzoic acid, β-alanine, and β-hydroxyaminobutyric acid.

The preferred amino acids suitable for use in the proteinaceous suds stabilizers of the present invention have the formula:



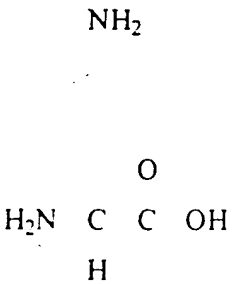
wherein R and R^1 are independently hydrogen or a moiety as describe herein above preferably R^1 is hydrogen and R comprise a moiety having a positive charge at a pH of from about 4 to about 12 wherein the polymers have an average cationic charge density of 2.77 or less, preferably of 2.75 or less, more preferably from about 0.01 to about 2.75, even more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12.

More preferred amino acids which comprise the proteinaceous suds stabilizers of the present invention have the formula:



wherein R hydrogen, C_1-C_6 linear or branched alkyl, C_1-C_6 substituted alkyl, and mixtures thereof. R is preferably C_1-C_6 substituted alkyl wherein preferred moieties which are substituted on said C_1-C_6 alkyl units include amino, hydroxy, carboxy, amido, thio, C_1-C_4 thioalkyl, 3-imidazolyl, 4-imidazolyl, 2-imidazolinyl, 4-imidazolinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1-pyrazolyl, 3-pyrazoyl, 4-pyrazoyl, 5-pyrazoyl, 1-pyrazolinyl, 3-pyrazolinyl, 4-pyrazolinyl, 5-pyrazolinyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, piperazinyl, 2-pyrrolidinyl, 3-pyrrolidinyl, guanidino, amidino, phenyl, substituted phenyl, wherein said phenyl substitution is hydroxy, halogen, amino, carboxy, and amido.

An example of a more preferred amino acid according to the present invention is the amino acid lysine having the formula:



wherein R is a substituted C_1 alkyl moiety, said substituent is 4-imidazolyl.

Non-limiting examples of preferred amino acids include alanine, arginine, asparagine, aspartic acid, cysteine, glutamine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tryptophan, tyrosine, valine, and mixtures thereof. The aforementioned amino acids are typically referred to as the "primary α-amino

acids", however, the proteinaceous suds stabilizers of the present invention may comprise any amino acid having an R unit which together with the aforementioned amino acids serves to adjust the cationic charge density of the proteinaceous suds stabilizers to a range of 2.77 or less, preferably of 2.75 or less, more preferably from about 0.01 to about 2.75, even more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12. For example, further non-limiting examples of amino acids include homoserine, hydroxyproline, norleucine, norvaline, ornithine, penicillamine, and phenylglycine, preferably ornithine. R units preferably comprise moieties which are capable of a cationic or anionic charges within the range of pH from about 4 to about 12. Non-limiting examples of preferred amino acids having anionic R units include glutamic acid, aspartic acid, and γ-carboxyglutamic acid.

For the purposes of the present invention, both optical isomers of any amino acid having a chiral center serve equally well for inclusion into the backbone of the peptide, polypeptide, or amino acid copolymers. Racemic mixtures of one amino acid may be suitably combined with a single optical isomer of one or more other amino acids depending upon the desired properties of the final proteinaceous suds stabilizer. The same applies to amino acids capable of forming diasteriomeric pairs, for example, threonine.

Nonlimiting examples of suitable proteinaceous suds stabilizers are described in PCT Application Serial No. PCT/US98/24707.

Polyamino Acid Proteinaceous Suds Stabilizer - One type of suitable proteinaceous suds stabilizer according to the present invention is comprised entirely of the amino acids described herein above. Said polyamino acid compounds may be naturally occurring peptides, polypeptides, enzymes, and the like, provided that the polymers have an average cationic charge density of 2.77 or less, preferably of 2.75 or less, more preferably from about 0.01 to about 2.75, even more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12. An example of a polyamino acid which is suitable as a proteinaceous suds stabilizer according to the present invention is the enzyme lysozyme.

An exception may, from time to time, occur in the case where naturally occurring enzymes, proteins, and peptides are chosen as proteinaceous suds stabilizers provided that the polymers have an average cationic charge density of 2.77 or less, preferably of 2.75 or less, more preferably from about 0.01 to about 2.75, even more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12.

Another class of suitable polyamino acid compound is the synthetic peptide having a molecular weight of at least about 1500 daltons. In addition, the polymers have an average

cationic charge density of 2.77 or less, preferably of 2.75 or less, more preferably from about 0.01 to about 2.75, even more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12. An example of a polyamino acid synthetic peptide suitable for use as a proteinaceous suds stabilizer according to the present invention is the copolymer of the amino acids lysine, alanine, glutamic acid, and tyrosine having an average molecular weight of 52,000 daltons and a ratio of lys:ala:glu:tyr of approximately 5:6:2:1.

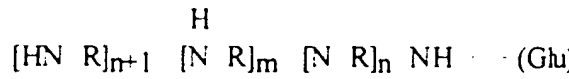
Without wishing to be limited by theory, the presence of one or more cationic amino acids, for example, histidine, ornithine, lysine and the like, is required to insure increased suds stabilization and suds volume. However, the relative amount of cationic amino acid present, as well as the average cationic charge density of the polyamino acid, are key to the effectiveness of the resulting material. For example, poly L-lysine having a molecular weight of approximately 18,000 daltons comprises 100% amino acids which have the capacity to possess a positive charge in the pH range of from about 4 to about 12, with the result that this material is ineffective as a suds extender and as a greasy soil removing agent.

Peptide Copolymers - Another class of materials suitable for use as proteinaceous suds stabilizers according to the present invention are peptide copolymers. For the purposes of the present invention "peptide copolymers" are defined as "polymeric materials with a molecular weight greater than or equal to about 1500 daltons wherein at least about 10% by weight of said polymeric material comprises one or more amino acids".

Peptide copolymers suitable for use as proteinaceous suds stabilizers may include segments of polyethylene oxide which are linked to segments of peptide or polypeptide to form a material which has increased suds retention as well as formulatability.

Nonlimiting examples of amino acid copolymer classes include the following.

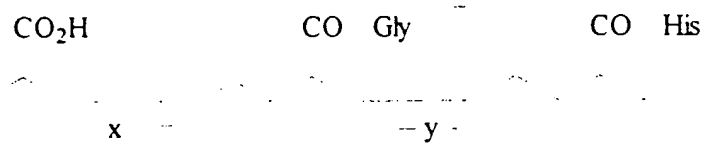
Polyalkyleneimine copolymers comprise random segments of polyalkyleneimine, preferably polyethyleneimine, together with segments of amino acid residues. For example, tetraethylenepentamine is reacted together with polyglutamic acid and polyalanine to form a copolymer having the formula:



wherein m is equal to 3, n is equal to 0, i is equal to 3, j is equal to 5, x is equal to 3, y is equal to 4, and z is equal to 7.

However, the formulator may substitute other polyamines for polyalkyleneimines, for example, polyvinyl amines, or other suitable polyamine which provides for a source of cationic charge at a pH of from 4 to abut 12 and which results in a copolymer having an average cationic charge density of 2.77 or less, preferably of 2.75 or less, more preferably from about 0.01 to about 2.75, even more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12.

The formulator may combine non-amine polymers with protonatable as well as non-protonatable amino acids. For example, a carboxylate-containing homo-polymer may be reacted with one or more amino acids, for example, histidine and glycine, to form an amino acid containing amido copolymer having the formula:

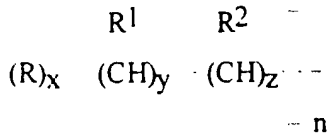


wherein said copolymer has a molecular weight of at least 1500 daltons and a ratio of x : y : z of approximately 2 : 3 : 6.

Zwitterionic Polymers

The polymeric suds stabilizers of the present invention are homopolymers or copolymers wherein the monomers which comprise said homopolymers or copolymers contain a moiety capable of being protonated at a pH of from about 4 to about 12, or a moiety capable of being de-protonated at a pH of from about 4 to about 12, of a mixture of both types of moieties.

A preferred class of zwitterionic polymers suitable for use as a suds volume and suds duration enhancer has the formula:



wherein R is C_1-C_{12} linear alkylene, C_1-C_{12} branched alkylene, and mixtures thereof; preferably C_1-C_4 linear alkylene, C_3-C_4 branched alkylene; more preferably methylene and 1,2-propylene. The index x is from 0 to 6; y is 0 or 1; z is 0 or 1.

The index n has the value such that the zwitterionic polymers of the present invention have an average molecular weight of from about 1,000 to about 2,000,000 preferably from about 5,000 to about 1,000,000, more preferably from about 10,000 to about 750,000, more preferably from about 20,000 to about 500,000, even more preferably from about 35,000 to about 300,000

daltons. The molecular weight of the polymeric suds boosters, can be determined via conventional gel permeation chromatography.

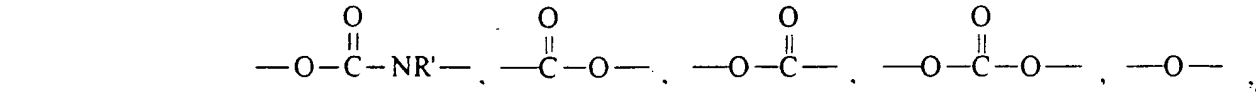
Nonlimiting examples of suitable zwitterionic polymers are described in PCT Application Serial No. PCT/US98/24699

Anionic Units

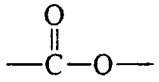
R^1 is a unit capable of having a negative charge at a pH of from about 4 to about 12. Preferred R^1 has the formula:

$$-(L)_i-(S)_j-R^3$$

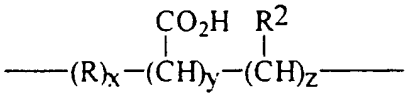
wherein L is a linking unit independently selected from the following:



and mixtures thereof, wherein R' is independently hydrogen, C_1-C_4 alkyl, and mixtures thereof; preferably hydrogen or alternatively R' and S can form a heterocycle of 4 to 7 carbon atoms, optionally containing other hetero atoms and optionally substituted. Preferably the linking group L can be introduced into the molecule as part of the original monomer backbone, for example, a polymer having L units of the formula:



can suitably have this moiety introduced into the polymer via a carboxylate containing monomer, for example, a monomer having the general formula:



When the index i is 0, L is absent.

For anionic units S is a "spacing unit" wherein each S unit is independently selected from C_1-C_{12} linear alkylene, C_1-C_{12} branched alkylene, C_3-C_{12} linear alkenylene, C_3-C_{12} branched alkenylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_6-C_{10} arylene, C_8-C_{12} dialkylarylene, $-(R^5O)_kR^5-$, $-(R^5O)_kR^6(OR^5)_k-$, $-CH_2CH(OR^7)CH_2-$, and mixtures thereof; wherein R^5 is C_2-C_4 linear alkylene, C_3-C_4 branched alkylene, and mixtures thereof, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene; R^6 is C_2-C_{12} linear

alkylene, and mixtures thereof, preferably ethylene; R^7 is hydrogen, C_1-C_4 alkyl, and mixtures thereof, preferably hydrogen. The index k is from 1 to about 20.

Preferably S is C_1-C_{12} linear alkylene, $-(R^5O)_kR^5-$, and mixtures thereof. When S is a $-(R^5O)_kR^5-$ unit, said units may be suitably formed by the addition an alkyleneoxy producing reactant (e.g. ethylene oxide, epichlorohydrin) or by addition of a suitable polyethyleneglycol. More preferably S is C_2-C_4 linear alkylene. When the index j is 0 the S unit is absent.

R^3 is independently selected from hydrogen, $-CO_2M$, $-SO_3M$, $-OSO_3M$, $-CH_2P(O)(OM)_2$, $-OP(O)(OM)_2$, units having the formula:

$$—CR^8R^9R^{10}$$

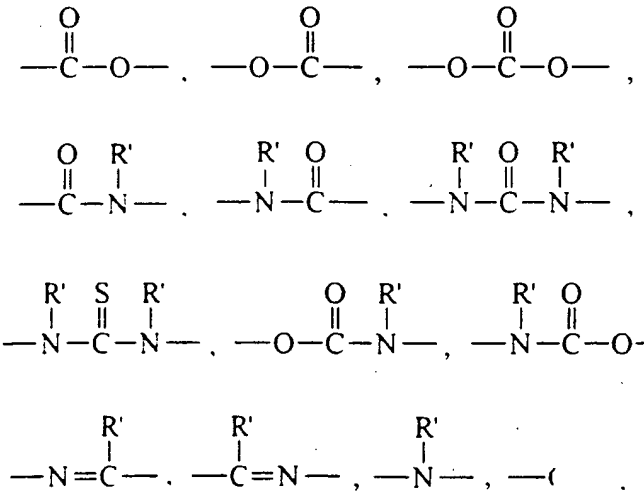
wherein each R^8, R^9, and R^{10} is independently selected from the group consisting of hydrogen, $-(CH_2)_mR^{11}$, and mixtures thereof, wherein R^{11} is $-CO_2H$, $-SO_3M$, $-OSO_3M$, $-CH(CO_2H)CH_2CO_2H$, $-CH_2P(O)(OH)_2$, $-OP(O)(OH)_2$, and mixtures thereof, preferably $-CO_2H$, $-CH(CO_2H)CH_2CO_2H$, and mixtures thereof, more preferably $-CO_2H$; provided that one R^8, R^9, or R^{10} is not a hydrogen atom, preferably two R^8, R^9, or R^{10} units are hydrogen. M is hydrogen or a salt forming cation, preferably hydrogen. The index m has the value from 0 to 10.

Cationic Units

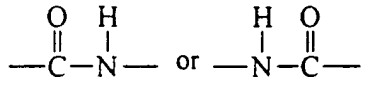
R^2 is a unit capable of having a positive charge at a pH of from about 4 to about 12. Preferred R^2 has the formula:

$$—(L^1)_i—(S)_j—R^4$$

wherein L^1 is a linking unit independently selected from the following:



and mixtures thereof; wherein R' is independently hydrogen, C_1-C_4 alkyl, and mixtures thereof; preferably hydrogen or alternatively R' and S can form a heterocycle of 4 to 7 carbon atoms, optionally containing other hetero atoms and optionally substituted. Preferably L^1 has the formula:



When the index i' is equal to 0, L^1 is absent.

For cationic units S is a "spacing unit" wherein each S unit is independently selected from C_1-C_{12} linear alkylene, C_1-C_{12} branched alkylene, C_3-C_{12} linear alkenylene, C_3-C_{12} branched alkenylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_6-C_{10} arylene, C_8-C_{12} dialkylarylene, $-(R^5O)_kR^5-$, $-(R^5O)_kR^6(OR^5)_k-$, $-CH_2CH(OR^7)CH_2-$, and mixtures thereof; wherein R^5 is C_2-C_4 linear alkylene, C_3-C_4 branched alkylene, and mixtures thereof, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene; R^6 is C_2-C_{12} linear alkylene, and mixtures thereof, preferably ethylene; R^7 is hydrogen, C_1-C_4 alkyl, and mixtures thereof, preferably hydrogen. The index k is from 1 to about 20.

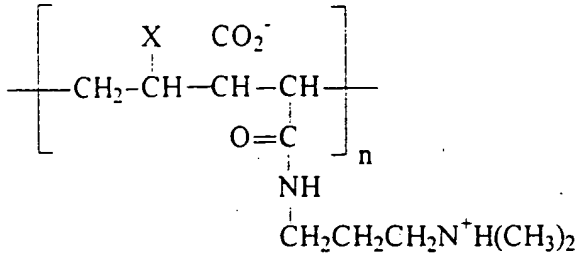
Preferably S is C_1-C_{12} linear alkylene, and mixtures thereof. Preferably S is C_2-C_4 linear alkylene. When the index j' is 0 the S unit is absent.

R^4 is independently selected from amino, alkylamino carboxamide, 3-imidazolyl, 4-imidazolyl, 2-imidazolinyl, 4-imidazolinyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1-pyrazolyl, 3-pyrazoyl, 4-pyrazoyl, 5-pyrazoyl, 1-pyrazolinyl, 3-pyrazolinyl, 4-pyrazolinyl, 5-pyrazolinyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, piperazinyl, 2-pyrrolidinyl, 3-pyrrolidinyl, guanidino, amidino, and mixtures thereof, preferably dialkylamino having the formula:

$$-N(R^{11})_2$$

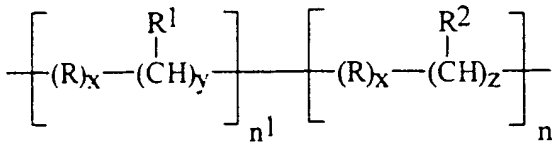
wherein each R^{11} is independently hydrogen, C_1-C_4 alkyl, and mixtures thereof, preferably hydrogen or methyl or alternatively the two R^{11} can form a heterocycle of 4 to 8 carbon atoms, optionally containing other hetero atoms and optionally substituted.

An example of a preferred zwitterionic polymer according to the present invention has the formula:



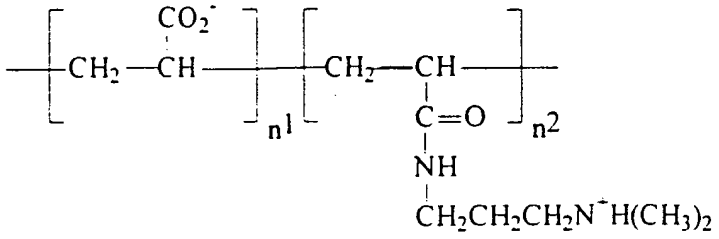
wherein X is C_6, n has a value such that the average molecular weight is from about 1,000 to about 2,000,000.

Further preferred zwitterionic polymers according to the present invention are polymers comprising monomers wherein each monomer has only cationic units or anionic units, said polymers have the formula:



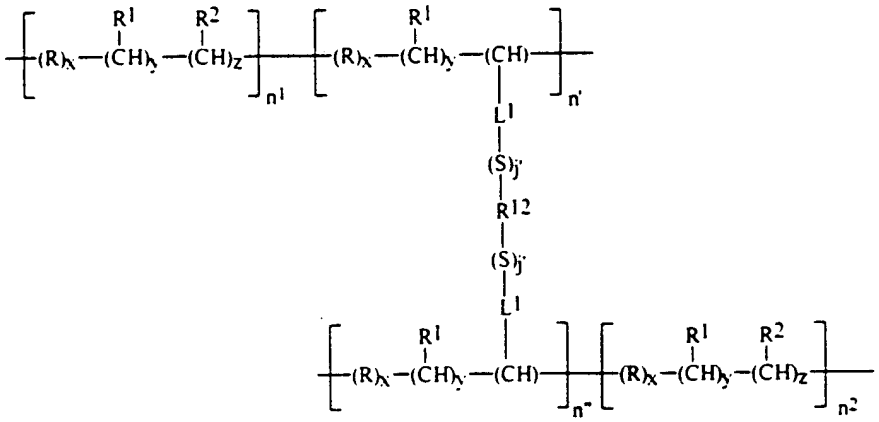
wherein R, R^1, x, y, and z are the same as defined herein above; $n^1 + n^2 = n$ such that n has a value wherein the resulting zwitterionic polymer has a molecular weight of form about 1,000 to about 2,000,000 daltons, provided that the resulting zwitterionic polymer has an average cationic charge density of 2.77 or less, preferably of 2.75 or less, more preferably from about 0.01 to about 2.75, even more preferably from about 0.1 to about 2.75, most preferably from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12.

An example of a polymer having monomers with only an anionic unit or a cationic unit has the formula:



wherein the sum of n^1 and n^2 provide a polymer with an average molecular weight of from about 1,000 to about 2,000,000 daltons.

Another preferred zwitterionic polymer according to the present invention are polymers which have limited crosslinking, said polymers having the formula:



wherein R, R^1, L^1, S, j', x, y, and z are the same as defined herein above; n' is equal to n", and the value n' + n" is less than or equal to 5% of the value of n^1 + n^2 = n; n provides a polymer with an average molecular weight of from about 1,000 to about 2,000,000 daltons. R^{12} is nitrogen, C_1-C_{12} linear alkylene amino alkylene having the formula:

$$-R^{13}\text{-}N\text{-}R^{13}\text{-}$$

L^1, and mixtures thereof, wherein each R^{13} is independently L^1 or ethylene.

The zwitterionic polymers of the present invention may comprise any combination of monomer units, for example, several different monomers having various R^1 and R^2 groups can be combined to form a suitable suds stabilizer. Alternatively the same R^1 unit may be used with a selection of different R^2 units and vice versa.

Cationic Charge Density

For the purposes of the present invention the term "cationic charge density" is defined as "the total number of units that are protonated at a specific pH per 100 daltons mass of polymer, or otherwise stated, the total number of charges divided by the dalton molecular weight of the monomer unit or polymer."

For illustrative purposes only, a polypeptide comprising 10 units of the amino acid lysine has a molecular weight of approximately 1028 daltons, wherein there are 11 $-NH_2$ units. If at a specific pH within the range of from about 4 to about 12, 2 of the $-NH_2$ units are protonated in the form of $-NH_3^+$, then the cationic charge density is 2 cationic charge units ÷ by 1028 daltons molecular weight = approximately 0.2 units of cationic charge per 100 daltons molecular weight. This would, therefore, have sufficient cationic charge to suffice the cationic charge density of the present invention, but insufficient molecular weight to be a suitable suds enhancer.

Polymers have been shown to be effective for delivering sudsing benefits in a hand dishwashing context, provided the polymer contains a cationic moiety, either permanent via a quaternary nitrogen or temporary via protonation. Without being limited by theory, it is believed

that the cationic charge must be sufficient to attract the polymer to negatively charged soils but not so large as to cause negative interactions with available anionic surfactants.

The cationic charge density may be determined as follows, where the cationic charge density is defined as the amount of cationic charge on a given polymer, either by permanent cationic groups or via protonated groups, as a weight percent of the total polymer at the desired wash pH. For example, with the terpolymer, DMAM/ hydroxyethylacrylate (HEA)/acrylic acid (AA) where the ratio of monomers is 1 mole of DMAM for 3 moles of HEA for 0.33 moles of AA, we have experimentally determined the pKa see hereinafter as to how pKa is measured, of this polymer to be 8.2. Thus, if the wash pH is 8.2, then half of the available nitrogens will be protonated (and count as cationic) and the other half will not be protonated (and not be counted in the "cationic charge density"). Thus, since the Nitrogen has a molecular weight of approximately 14 grams/mole, the DMAM monomer has a molecular weight of approximately 157 grams/mole, the HEA monomer has a molecular weight of approximately 116 grams/mole, and the AA monomer has a molecular weight of approximately 72 grams/mole, the cationic charge density can be calculated as follows:

Cationic Charge Density = (14/157+116+116+116+72) * 50% = 0.0132 or 1.32%.

Thus, 1.32% of the polymer contains cationic charges. Otherwise stated, the cationic charge density is 1.32 per 100 daltons molecular weight.

As another example, one could make a copolymer of DMAM with hydroxyethylacrylate (HEA), where the ratio of monomers is 1 mole of DMAM for 3 moles of HEA. The DMAM monomer has a molecular weight of approximately 157 and the HEA monomer has a molecular weight of 116 grams/mole. In this case the pKa has been measured to be 7.6. Thus, if the wash pH is 5.0, all of the available nitrogens will be protonated. The cationic charge density is then calculated:

Cationic Charge Density = 14/(157+116+116+116) * 100% = 0.0277, or 2.77%.

Thus, the cationic charge density is 2.77 per 100 daltons molecular weight. Notice that in this example, the minimum repeating unit is considered 1 DMAM monomer plus 3 HEA monomers.

Alternatively, the cationic charge density can be determined as follows: where the cationic charge density is defined as the total number of charges divided by the dalton molecular weight of the polymer at the desired wash pH. It can be calculated from the following equation

$$\text{Cationic Charge Density} = \frac{\sum_i n_i f_i C_i}{\sum_j m_j}$$

where n_i is the number of charged unit. f_i is the fraction of unit being charged. In the case of protonated species (AH^+), f_i can be calculated from the measured pH and pKa.

$$f_{(AH^+)} = \frac{10^{pKa-pH}}{1+10^{pKa-pH}}$$

In the case of deprotonated anionic species (A^-)

$$f_{(A^-)} = \frac{10^{pH-pKa}}{1+10^{pH-pKa}}$$

C_i is the charge of the unit, m_j is the dalton molecular weight of the individual monomer units.

For example, with polyDMAM, we have experimentally determined the pKa, see hereinafter as to how pKa is measured, of this polymer to be 7.7. Thus, if the wash pH is 7.7, then half of the available nitrogens will be protonated (and count as cationic) $f_{(AH^+)} = 0.5$ and the other half will not be protonated (and not be counted in the " cationic charge density"). Thus, since the DMAM monomer has a molecular weight of approximately 157 grams/mole, the cationic charge density can be calculated:

Cationic Charge Density = (1*0.5/157) = 0.00318 or 0.318%.

Thus, at the wash pH of 7.7, polyDMAM has a cationic charge density of 0.318 charge per 100 dalton molecular weight. As another example, one could make a copolymer of DMAM with DMA, where the ratio of monomers is 1 mole of DMAM for 3 moles of DMA. The DMA monomer has a molecular weight of 99 grams/mole. In this case the pKa has been measured to be 7.6. Thus, if the wash pH is 5.0, all of the available nitrogens will be protonated. The cationic charge density is then calculated:

Cationic Charge Density = 1/(157+99+99+99) = 0.0022, or 0.22%.

At the wash pH of 5.0, a copolymer of DMAM with DMA has a charge density of 0.22 charge per 100 dalton molecular weight. Notice that in this example, the minimum repeating unit is considered 1 DMAM monomer plus 3 DMA monomers.

A key aspect of this calculation is the pKa measurement for any protonatable species which will result in a cationic charge on the heteroatom. Since the pKa is dependent on the polymer structure and various monomers present, this must be measure to determine the percentage of protonatable sites to count as a function of the desired wash pH. This is an easy exercise for one skilled in the art. Based on this calculation, the percent of cationic charge is independent of polymer molecular weight.

The pKa of a polymeric suds booster is determined in the following manner. Make at least 50 mls of a 5% polymer solution, such as a polymer prepared according to any of Examples 1 to 5 as described hereinafter, in ultra pure water(i.e. no added salt). At 25° C, take initial pH of the 5% polymer solution with a pH meter and record when a steady reading is achieved. Maintain temperature throughout the test at 25° C with a water bath and stir continuously. Raise pH of 50 mls of the aqueous polymer solution to 12 using NaOH (1N, 12.5M). Titrate 5 mls of 0.1N HCl into the polymer solution. Record pH when steady reading is achieved. Repeat steps 4 and 5 until pH is below 3. The pKa was determined from a plot of pH vs. volume of titrant using the standard procedure as disclosed in Quantitative Chemical Analysis, Daniel C. Harris, W.H. Freeman & Chapman, San Francisco, USA 1982.

It has been surprisingly found that when a polymeric suds booster of the present invention is at its optimum charge density, then reducing the molecular weight of the polymeric suds booster increases sudsing performance even in the presence of composite and/or greasy soils. Accordingly, then the polymeric suds booster is at its optimum charge density, the molecular weight of the polymeric suds booster, as determined in the manner described hereinbefore, is preferably in the range of from about 1,000 to about 2,000,000, more preferably from about 5,000 to about 500,000, even more preferably from about 10,000 to about 100,000, most preferably from about 20,000 to about 50,000 daltons.

The liquid detergent compositions according to the present invention comprise at least an effective amount of one or more polymeric suds stabilizers described herein, preferably from about 0.01% to about 10%, more preferably from about 0.001% to about 5%, most preferably from about 0.1% to about 2% by weight, of said composition. What is meant herein by "an effective amount of polymeric suds stabilizer" is that the suds produced by the presently described compositions are sustained for an increased amount of time relative to a composition which does not comprise a polymeric suds stabilizer described herein.

Detersive Surfactants

Anionic Surfactants - The anionic surfactants useful in the present invention are preferably selected from the group consisting of, linear alkylbenzene sulfonate, alpha olefin sulfonate, paraffin sulfonates, alkyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfate, alkyl sulfonates, alkyl alkoxy carboxylate, alkyl alkoxylated sulfates, sarcosinates, taurinates, and mixtures thereof.

An effective amount, typically from about 0.5% to about 90%, preferably about 5% to about 60%, more preferably from about 10 to about 30%, by weight of anionic detersive surfactant can be used in the present invention.

Alkyl sulfate surfactants are another type of anionic surfactant of importance for use herein. In addition to providing excellent overall cleaning ability when used in combination with polyhydroxy fatty acid amides (see below), including good grease/oil cleaning over a wide range of temperatures, wash concentrations, and wash times, dissolution of alkyl sulfates can be obtained, as well as improved formulability in liquid detergent formulations are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali (Group IA) metal cation (e.g., sodium, potassium, lithium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the like. Typically, alkyl chains of C_{12-16} are preferred for lower wash temperatures (e.g., below about 50°C) and C_{16-18} alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

Alkyl alkoxylated sulfate surfactants are another category of useful anionic surfactant. These surfactants are water soluble salts or acids typically of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperidinium and cations derived from alkanolamines, e.g. monoethanolamine, diethanolamine, and triethanolamine, and mixtures thereof. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate, C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate, C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate, and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate wherein M is conveniently selected from sodium and potassium. Surfactants for use herein can be made from natural or synthetic alcohol feedstocks. Chain lengths represent average hydrocarbon distributions, including branching.

Examples of suitable anionic surfactants are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also

generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

Secondary Surfactants - Secondary detersive surfactant can be selected from the group consisting of nonionics, cationics, ampholytics, zwitterionics, and mixtures thereof. By selecting the type and amount of detersive surfactant, along with other adjunct ingredients disclosed herein, the present detergent compositions can be formulated to be used in the context of laundry cleaning or in other different cleaning applications, particularly including dishwashing. The particular surfactants used can therefore vary widely depending upon the particular end-use envisioned. Suitable secondary surfactants are described below. Examples of suitable nonionic, cationic amphoteric and zwitterionic surfactants are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch).

Nonionic Detergent Surfactants - Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column 13, line 14 through column 16, line 6, incorporated herein by reference. Exemplary, non-limiting classes of useful nonionic surfactants include: amine oxides, alkyl ethoxylate, alkanoyl glucose amide, alkyl betaines, sulfobetaine and mixtures thereof.

Amine oxides are semi-polar nonionic surfactants and include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula

$$R^3(OR^4)_xN(R^5)_2 \rightarrow O$$

wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{12} alkoxy ethyl dihydroxy ethyl amine oxides. Preferably the amine oxide is present in the composition in an effective amount, more preferably from about 0.1% to about 20%, even more preferably about 0.1% to about 15%, even more preferably still from about 0.5% to about 10%,by weight.

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide. In a preferred embodiment the ethylene oxide is present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal® CO-630, marketed by the GAF Corporation; and Triton® X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company. These compounds are commonly referred to as alkyl phenol alkoxylates, (e.g., alkyl phenol ethoxylates).

The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 18 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol® 15-S-9 (the condensation product of C_{11}-C_{15} linear secondary alcohol with 9 moles ethylene oxide), Tergitol® 24-L-6 NMW (the condensation product of C_{12}-C_{14} primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol® 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol® 23-6.5 (the condensation product of C_{12}-C_{13} linear alcohol with 6.5 moles of ethylene oxide), Neodol® 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide), Neodol® 45-4 (the condensation product of C_{14}-C_{15} linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro® EOB (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company. Other commercially available nonionic surfactants include Dobanol 91-8® marketed by Shell Chemical Co. and Genapol UD-080® marketed by Hoechst. This category of nonionic surfactant is referred to generally as "alkyl ethoxylates."

The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)_t(\text{glycosyl})_x$$

wherein R^2 is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

Fatty acid amide surfactants having the formula:

$$R^6\overset{O}{\overset{\|}{C}}N(R^7)_2$$

wherein R^6 is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and $-(C^2H_4O)_xH$ where x varies from about 1 to about 3.

Preferred amides are C_8-C_{20} ammonia amides, monoethanolamides, diethanolamides, and isopropanolamides.

Preferably the nonionic surfactant, when present in the composition, is present in an effective amount, more preferably from about 0.1% to about 20%, even more preferably about 0.1% to about 15%, even more preferably still from about 0.5% to about 10%,by weight.

Polyhydroxy Fatty Acid Amide Surfactant - The detergent compositions hereof may also contain an effective amount of polyhydroxy fatty acid amide surfactant. By "effective amount" is meant that the formulator of the composition can select an amount of polyhydroxy fatty acid amide to be incorporated into the compositions that will improve the cleaning performance of the detergent composition. In general, for conventional levels, the incorporation of about 1%, by weight, polyhydroxy fatty acid amide will enhance cleaning performance.

The detergent compositions herein will typically comprise about 1% weight basis, polyhydroxy fatty acid amide surfactant, preferably from about 3% to about 30%, of the polyhydroxy fatty acid amide. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:

$$R^2\overset{O}{\overset{\|}{C}}N\overset{|}{R^1}$$

wherein: R^1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C_1-C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl);

and R^2 is a C_5-C_{31} hydrocarbyl, preferably straight chain C_7-C_{19} alkyl or alkenyl, more preferably straight chain C_9-C_{17} alkyl or alkenyl, most preferably straight chain C_{11}-C_{15} alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-CH_2-(CHOH)_n-CH_2OH$, $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2OH$, $-CH_2-(CHOH)_2(CHOR')(CHOH)-CH_2OH$, and alkoxylated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly $-CH_2-(CHOH)_4-CH_2OH$.

R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

R^2-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

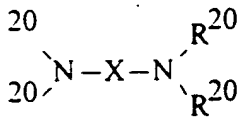
Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriotityl, etc.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

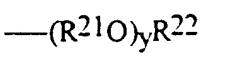
Diamines

The preferred liquid detergent compositions of the present invention further comprise one or more diamines, preferably an amount of diamine such that the ratio of anionic surfactant present to the diamine is from about 40 : 1 to about 2: 1. Said diamines provide for increased removal of grease and greasy food material while maintaining suitable levels of suds.

The diamines suitable for use in the compositions of the present invention have the formula:

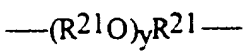


wherein each R^{20} is independently selected from the group consisting of hydrogen, C_1-C_4 linear or branched alkyl, alkyleneoxy having the formula:



wherein R^{21} is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^{22} is hydrogen, C_1-C_4 alkyl, and mixtures thereof; y is from 1 to about 10; X is a unit selected from:

i) C_3-C_{10} linear alkylene, C_3-C_{10} branched alkylene, C_3-C_{10} cyclic alkylene, C_3-C_{10} branched cyclic alkylene, an alkyleneoxyalkylene having the formula:



wherein R^{21} and y are the same as defined herein above;

ii) C_3-C_{10} linear, C_3-C_{10} branched linear, C_3-C_{10} cyclic, C_3-C_{10} branched cyclic alkylene, C_6-C_{10} arylene, wherein said unit comprises one or more electron donating or electron withdrawing moieties which provide said diamine with a pK_a greater than about 8; and

iii) mixtures of (i) and (ii)

provided said diamine has a pK_a of at least about 8.

The preferred diamines of the present invention have a pK_1 and pK_2 which are each in the range of from about 8 to about 11.5, preferably in the range of from about 8.4 to about 11, more preferably from about 8.6 to about 10.75. For the purposes of the present invention the term "pK_a" stands equally well for the terms "pK_1" and "pK_2" either separately or collectively. The term pK_a as used herein throughout the present specification in the same manner as used by those of ordinary skill in the art. pK_a values are readily obtained from standard literature sources, for example, "Critical Stability Constants: Volume 2, Amines" by Smith and Martel, Plenum Press, N.Y. and London, (1975).

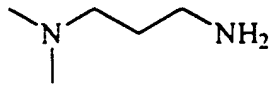
As an applied definition herein, the pK_a values of the diamines are specified as being measured in an aqueous solution at 25° C having an ionic strength of from about 0.1 to about 0.5 M. As used herein, the pK_a is an equilibrium constant dependent upon temperature and ionic strength, therefore, value reported by literature references, not measured in the above described manner, may not be within full agreement with the values and ranges which comprise the present invention. To eliminate ambiguity, the relevant conditions and/or references used for pK_a's of

this invention are as defined herein or in "Critical Stability Constants: Volume 2, Amines". One typical method of measurement is the potentiometric titration of the acid with sodium hydroxide and determination of the pK_a by suitable methods as described and referenced in "The Chemist's Ready Reference Handbook" by Shugar and Dean, McGraw Hill, NY, 1990.

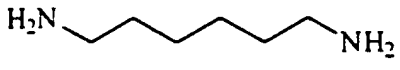
Preferred diamines for performance and supply considerations are 1,3-bis(methylamino)cyclohexane. 1,3-diaminopropane (pK_1=10.5; pK_2=8.8), 1,6-diaminohexane (pK_1=11; pK_2=10), 1,3-diaminopentane (Dytek EP) (pK_1=10.5; pK_2=8.9), 2-methyl 1,5-diaminopentane (Dytek A) (pK_1=11.2; pK_2=10.0). Other preferred materials are the primary/primary diamines having alkylene spacers ranging from C_4-C_8. In general, primary diamines are preferred over secondary and tertiary diamines.

The following are non-limiting examples of diamines suitable for use in the present invention.

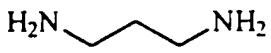
1-N,N-dimethylamino-3-aminopropane having the formula:



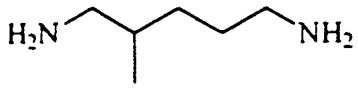
1,6-diaminohexane having the formula:



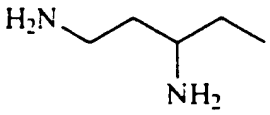
1,3-diaminopropane having the formula:



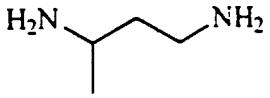
2-methyl-1,5-diaminopentane having the formula:



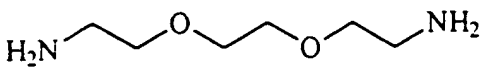
1,3-diaminopentane, available under the tradename Dytek EP, having the formula:



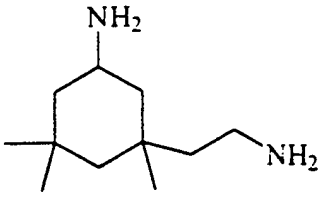
1,3-diaminobutane having the formula:



Jeffamine EDR 148, a diamine having an alkyleneoxy backbone, having the formula:

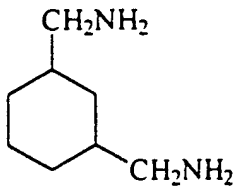


3-methyl-3-aminoethyl-5-dimethyl-1-aminocyclohexane (isophorone diamine) having the formula:



, and

1,3-bis(methylamino)cyclohexane having the formula:



ADJUNCT INGREDIENTS

Builder - The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylene-diamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylene-phosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula R-CH(COOH)CH_2(COOH) wherein R is C10-20 alkyl or alkenyl, preferably C12-16, or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substituents. Specific examples include lauryl succinate , myristyl succinate, palmityl succinate 2-dodecenylsuccinate, 2-tetradecenyl succinate. Succinate

builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

Especially for the liquid execution herein, suitable fatty acid builders for use herein are saturated or unsaturated C10-18 fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid. Other preferred builder system for liquid compositions is based on dodecenyl succinic acid and citric acid.

Detergency builder salts are normally included in amounts of from 3% to 50% by weight of the composition preferably from 5% to 30% and most usually from 5% to 25% by weight.

OPTIONAL DETERGENT INGREDIENTS

Enzymes - Detergent compositions of the present invention may further comprise one or more enzymes which provide cleaning performance benefits. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases, arabinosidases or mixtures thereof. A preferred combination is a detergent composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase. Enzymes when present in the compositions, at from about 0.0001% to about 5% of active enzyme by weight of the detergent composition.

Proteolytic Enzyme - The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. The proteases for use in the detergent compositions herein include (but are not limited to) trypsin, subtilisin, chymotrypsin and elastase-type proteases. Preferred for use herein are subtilisin-type proteolytic enzymes. Particularly preferred is bacterial serine proteolytic enzyme obtained from Bacillus subtilis and/or Bacillus licheniformis.

Suitable proteolytic enzymes include Novo Industri A/S Alcalase® (preferred), Esperase®, Savinase® (Copenhagen, Denmark), Gist-brocades' Maxatase®, Maxacal® and Maxapem 15® (protein engineered Maxacal®) (Delft, Netherlands), and subtilisin BPN and BPN'(preferred), which are commercially available. Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those made by Genencor International, Inc. (San Francisco, California) which are described in European Patent 251,446B, granted December 28, 1994 (particularly pages 17, 24 and 98) and which are also called herein "Protease B". U.S. Patent 5,030,378, Venegas, issued July 9, 1991, refers to a modified bacterial serine proteolytic enzyme (Genencor International) which is called "Protease A" herein (same as BPN'). In particular see columns 2 and 3 of U.S. Patent 5,030,378 for a complete description, including amino sequence, of Protease

A and its variants. Other proteases are sold under the tradenames: Primase, Durazym, Opticlean and Optimase. Preferred proteolytic enzymes, then, are selected from the group consisting of Alcalase ® (Novo Industri A/S), BPN', Protease A and Protease B (Genencor), and mixtures thereof. Protease B is most preferred.

Of particular interest for use herein are the proteases described in U.S. Patent No. 5,470,733.

Also proteases described in our co-pending application USSN 08/136,797 can be included in the detergent composition of the invention.

Another preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of Bacillus amyloliquefaciens subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International (A. Baeck et al. entitled "Protease-Containing Cleaning Compositions" having U.S. Serial No. 08/322,676, filed October 13, 1994).

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Other particularly useful proteases are multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at an amino acid residue position corresponding to position 103 of *Bacillus amyloliquefaciens* subtilisin in combination with a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 1, 3, 4, 8, 9, 10, 12, 13, 16, 17, 18, 19, 20, 21, 22, 24, 27, 33, 37, 38, 42, 43, 48, 55, 57, 58, 61, 62, 68, 72, 75, 76, 77, 78, 79, 86, 87, 89, 97, 98, 99, 101, 102, 104, 106, 107, 109, 111, 114, 116, 117, 119, 121, 123, 126, 128, 130, 131, 133, 134, 137, 140, 141, 142, 146, 147, 158, 159, 160, 166, 167, 170, 173, 174, 177, 181, 182, 183, 184, 185, 188, 192, 194, 198, 203, 204, 205, 206, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 222, 224, 227, 228, 230, 232, 236, 237, 238, 240, 242, 243, 244, 245, 246, 247, 248, 249, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 265, 268, 269, 270, 271, 272, 274 and 275 of *Bacillus amyloliquefaciens* subtilisin; wherein when said protease variant includes a substitution of amino acid residues at positions corresponding to positions 103 and 76, there is also a substitution of an amino acid residue at one

or more amino acid residue positions other than amino acid residue positions corresponding to positions 27, 99, 101, 104, 107, 109, 123, 128, 166, 204, 206, 210, 216, 217, 218, 222, 260, 265 or 274 of *Bacillus amyloliquefaciens* subtilisin and/or multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 62, 212, 230, 232, 252 and 257 of *Bacillus amyloliquefaciens* subtilisin as described in PCT Published Application Nos. WO 99/20727, WO 99/20726, and WO 99/20723 all owned by The Procter & Gamble Company.

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

Commercially available proteases useful in the present invention are known as ESPERASE®, ALCALASE®, DURAZYM®, SAVINASE®, EVERLASE® and KANNASE® all from Novo Nordisk A/S of Denmark, and as MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® all from Genencor International (formerly Gist-Brocades of The Netherlands).

Protease enzymes may be incorporated into the compositions in accordance with the present invention at a level of from about 0.0001% to about 2% active enzyme by weight of the composition.

Bleach/amylase/protease combinations (EP 755,999 A; EP 756,001 A; EP 756,000 A) are also useful.

Also in relation to enzymes herein, enzymes and their directly linked inhibitors, e.g., protease and its inhibitor linked by a peptide chain as described in WO 98/13483 A, are useful in conjunction with the present hybrid builders. Enzymes and their non-linked inhibitors used in selected combinations herein include protease with protease inhibitors selected from proteins, peptides and peptide derivatives as described in WO 98/13461 A, WO 98/13460 A, WO 98/13458 A, WO 98/13387 A.

Amylases can be used with amylase antibodies as taught in WO 98/07818 A and WO 98/07822 A, lipases can be used in conjunction with lipase antibodies as taught in WO 98/07817 A and WO 98/06810 A, proteases can be used in conjunction with protease antibodies as taught in

WO 98/07819 A and WO 98/06811 A. Cellulase can be combined with cellulase antibodies as taught in WO 98/07823 A and WO 98/07821 A. More generally, enzymes can be combined with similar or dissimilar enzyme directed antibodies, for example as taught in WO 98/07820 A or WO 98/06812 A.

The preferred enzymes herein can be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin.

Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Amylases (α and/or ß) can be included for removal of carbohydrate-based stains. WO94/02597 describes laundry compositions which incorporate mutant amylases. See also WO95/10603. Other amylases known for use in laundry compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314 and WO96/05295, Genencor, and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603. Also suitable are amylases described in EP 277 216.

Examples of commercial α-amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban® ,Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25° C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The compositions of the present invention may also comprise a mannanase enzyme. Preferably, the mannanase is selected from the group consisting of: three mannans-degrading enzymes : EC 3.2.1.25 : β-mannosidase, EC 3.2.1.78 : Endo-1,4-β-mannosidase, referred therein after as "mannanase" and EC 3.2.1.100 : 1,4-β-mannobiosidase and mixtures thereof. (IUPAC Classification- Enzyme nomenclature, 1992 ISBN 0-12-227165-3 Academic Press).

More preferably, the treating compositions of the present invention, when a mannanase is present, comprise a β-1,4-Mannosidase (E.C. 3.2.1.78) referred to as Mannanase. The term "mannanase" or "galactomannanase" denotes a mannanase enzyme defined according to the art as officially being named mannan endo-1,4-beta-mannosidase and having the alternative names beta-mannanase and endo-1,4-mannanase and catalysing

the reaction: random hydrolysis of 1,4-beta-D- mannosidic linkages in mannans, galactomannans, glucomannans, and galactoglucomannans.

In particular, Mannanases (EC 3.2.1.78) constitute a group of polysaccharases which degrade mannans and denote enzymes which are capable of cleaving polyose chains contaning mannose units, i.e. are capable of cleaving glycosidic bonds in mannans, glucomannans, galactomannans and galactogluco-mannans. Mannans are polysaccharides having a backbone composed of β-1,4- linked mannose; glucomannans are polysaccharides having a backbone or more or less regularly alternating β-1,4 linked mannose and glucose; galactomannans and galactoglucomannans are mannans and glucomannans with α-1,6 linked galactose sidebranches. These compounds may be acetylated.

The degradation of galactomannans and galactoglucomannans is facilitated by full or partial removal of the galactose sidebranches. Further the degradation of the acetylated mannans, glucomannans, galactomannans and galactogluco-mannans is facilitated by full or partial deacetylation. Acetyl groups can be removed by alkali or by mannan acetylesterases. The oligomers which are released from the mannanases or by a combination of mannanases and α-galactosidase and/or mannan acetyl esterases can be further degraded to release free maltose by β-mannosidase and/or β-glucosidase.

Mannanases have been identified in several *Bacillus* organisms. For example, Talbot et al., Appl. Environ. Microbiol., Vol.56, No. 11, pp. 3505-3510 (1990) describes a beta-mannanase derived from *Bacillus stearothermophilus* in dimer form having molecular weight of 162 kDa and an optimum pH of 5.5-7.5. Mendoza et al., World J. Microbiol. Biotech., Vol. 10, No. 5, pp. 551-555 (1994) describes a beta-mannanase derived from *Bacillus subtilis* having a molecular weight of 38 kDa, an optimum activity at pH 5.0 and 55C and a pI of 4.8. JP-03047076 discloses a beta-mannanase derived from *Bacillus* sp., having a molecular weight of 373 kDa measured by gel filtration, an optimum pH of 8-10 and a pI of 5.3-5.4. JP-63056289 describes the production of an alkaline, thermostable beta-mannanase which hydrolyses beta-1,4-D-mannopyranoside bonds of e.g. mannans and produces manno-oligosaccharides. JP-63036774 relates to the *Bacillus* microorganism FERM P-8856 which produces beta-mannanase and beta-mannosidase at an alkaline pH. JP-08051975 discloses alkaline beta-mannanases from alkalophilic *Bacillus* sp. AM-001. A purified mannanase from *Bacillus amyloliquefaciens* useful in the bleaching of pulp and paper and a method of preparation thereof is disclosed in WO 97/11164. WO 91/18974 describes a hemicellulase such as a glucanase, xylanase or mannanase active at an extreme pH and temperature. WO 94/25576 discloses an enzyme from *Aspergillus aculeatus*, CBS 101.43, exhibiting mannanase activity which

may be useful for degradation or modification of plant or algae cell wall material. WO 93/24622 discloses a mannanase isolated from *Trichoderma reseei* useful for bleaching lignocellulosic pulps. An hemicellulase capable of degrading mannan-containing hemicellulose is described in WO91/18974 and a purified mannanase from *Bacillus amyloliquefaciens* is described in WO97/11164.

Preferably, the mannanase enzyme will be an alkaline mannanase as defined below, more preferably, a mannanase originating from a bacterial source. Especially, the laundry detergent composition of the present invention will comprise an alkaline mannanase selected from the mannanase from the strain *Bacillus agaradhaerens* NICMB 40482; the mannanase from *Bacillus subtilis* strain 168, gene yght; the mannanase from *Bacillus sp.* I633 and/or the mannanase from *Bacillus sp.* AAI12. Most preferred mannanase for the inclusion in the detergent compositions of the present invention is the mannanase enzyme originating from *Bacillus sp.* I633 as described in the co-pending Danish patent application No. PA 1998 01340.

The terms "alkaline mannanase enzyme" is meant to encompass an enzyme having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its maximum activity at a given pH ranging from 7 to 12, preferably 7.5 to 10.5.

The alkaline mannanase from *Bacillus agaradhaerens* NICMB 40482 is described in the co-pending U.S. patent application serial No. 09/111,256. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus agaradhaerens*, NCIMB 40482; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 32-343 of SEQ ID NO:2 as shown in U.S. patent application serial No. 09/111,256; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 97 to nucleotide 1029 as shown in U.S. patent application serial No. 09/111,256;

(b) species homologs of (a):

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 32 to amino acid residue 343 as shown in U.S. patent application serial No. 09/111,256;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pSJ1678 comprising the polynucleotide molecule (the DNA sequence) encoding said mannanase has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 18 May 1998 under the deposition number DSM 12180.

A second more preferred enzyme is the mannanase from the *Bacillus subtilis* strain 168, which is described in the co-pending U.S. patent application serial No. 09/095,163. More specifically, this mannanase is:

i) is encoded by the coding part of the DNA sequence shown in SED ID No. 5 shown in the U.S. patent application serial No. 09/095,163 or an analogue of said sequence; and/or

ii) a polypeptide comprising an amino acid sequence as shown SEQ ID NO:6 shown in the U.S. patent application serial No. 09/095,163; or

iii) an analogue of the polypeptide defined in ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed in the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO:5 as shown in the U.S. patent application serial No. 09/095,163

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid

sequence of SEQ ID NO: 6 as shown in the U.S. patent application serial No. 09/095,163;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

A third more preferred mannanase is described in the co-pending Danish patent application No. PA 1998 01340. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus sp.* 1633;

ii) a polypeptide comprising an amino acid sequence as shown in positions 33-340 of SEQ ID NO:2 as shown in the Danish application No. PA 1998 01340; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of:

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 317 to nucleotide 1243 the Danish application No. PA 1998 01340;

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 33 to amino acid residue 340 the Danish application No. PA 1998 01340;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM3 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 29 May 1998 under the deposition number DSM 12197.

A fourth more preferred mannanase is described in the Danish co-pending patent application No. PA 1998 01341. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus sp.* AAI 12;

ii) a polypeptide comprising an amino acid sequence as shown in positions 25-362 of SEQ ID NO:2as shown in the Danish application No. PA 1998 01341; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 225 to nucleotide 1236 as shown in the Danish application No. PA 1998 01341;

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 25 to amino acid residue 362 as shown in the Danish application No. PA 1998 01341;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM1 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 7 October 1998 under the deposition number DSM 12433.

The mannanase, when present, is incorporated into the treating compositions of the present invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition.

The compositions of the present invention may also comprise a xyloglucanase enzyme. Suitable xyloglucanases for the purpose of the present invention are enzymes

exhibiting endoglucanase activity specific for xyloglucan, preferably at a level of from about 0.001% to about 1%, more preferably from about 0.01% to about 0.5%, by weight of the composition. As used herein, the term "endoglucanase activity" means the capability of the enzyme to hydrolyze 1,4-β-D-glycosidic linkages present in any cellulosic material, such as cellulose, cellulose derivatives, lichenin, β-D-glucan, or xyloglucan. The endoglucanase activity may be determined in accordance with methods known in the art, examples of which are described in WO 94/14953 and hereinafter. One unit of endoglucanase activity (e.g. CMCU, AVIU, XGU or BGU) is defined as the production of 1 μmol reducing sugar/min from a glucan substrate, the glucan substrate being, e.g., CMC (CMCU), acid swollen Avicell (AVIU), xyloglucan (XGU) or cereal β-glucan (BGU). The reducing sugars are determined as described in WO 94/14953 and hereinafter. The specific activity of an endoglucanase towards a substrate is defined as units/mg of protein.

Suitable are enzymes exhibiting as its highest activity XGU endoglucanase activity (hereinafter "specific for xyloglucan"), which enzyme:

i) is encoded by a DNA sequence comprising or included in at least one of the following partial sequences

(a) ATTCATTTGT GGACAGTGGA C (SEQ ID No: 1)

(b) GTTGATCGCA CATTGAACCA (SEQ ID NO: 2)

(c) ACCCCAGCCG ACCGATTGTC (SEQ ID NO: 3)

(d) CTTCCTTACC TCACCATCAT (SEQ ID NO: 4)

(e) TTAACATCTT TTCACCATGA (SEQ ID NO: 5)

(f) AGCTTTCCCT TCTCTCCCTT (SEQ ID NO: 6)

(g) GCCACCCTGG CTTCCGCTGC CAGCCTCC (SEQ ID NO: 7)

(h) GACAGTAGCA ATCCAGCATT (SEQ ID NO: 8)

(i) AGCATCAGCC GCTTTGTACA (SEQ ID NO: 9)

(j) CCATGAAGTT CACCGTATTG (SEQ ID NO: 10)

(k) GCACTGCTTC TCTCCCAGGT (SEQ ID NO: 11)

(l) GTGGGCGGCC CCTCAGGCAA (SEQ ID NO: 12)

(m) ACGCTCCTCC AATTTTCTCT (SEQ ID NO: 13)

(n) GGCTGGTAG TAATGAGTCT (SEQ ID NO: 14)

(o) GGCGCAGAGT TTGGCCAGGC (SEQ ID NO: 15)

(p) CAACATCCCC GGTGTTCTGG G (SEQ ID NO: 16)

(q) AAAGATTCAT TTGTGGACAG TGGACGTTGA TCGCACATTG AACCAACCCC AGCCGACCGA

TTGTCCTTCC TTACCTCACC ATCATTTAAC ATCTTTTCAC CATGAAGCTT TCCCTTCTCT
CCCTTGCCAC CCTGGCTTCC GCTGCCAGCC TCCAGCGCCG CACACTTCTG CGGTCAGTGG
GATACCGCCA CCGCCGGTGA CTTCACCCTG TACAACGACC TTTGGGGCGA GACGGCCGGC
ACCGGCTCCC AGTGCACTGG AGTCGACTCC TACAGCGGCG ACACCATCGC TTGTCACACC
AGCAGGTCCT GGTCGGAGTA GCAGCAGCGT CAAGAGCTAT GCCAACG (SEQ ID NO:17) or

(r) CAGCATCTCC ATTGAGTAAT CACGTTGGTG TTCGGTGGCC CGCCGTGTTG CGTGGCGGAG
GCTGCCGGGA GACGGGTGGG GATGGTGGTG GGAGAGAATG TAGGGCGCCG TGTTTCAGTC
CCTAGGCAGG ATACCGGAAA ACCGTGTGGT AGGAGGTTTA TAGGTTTCCA GGAGACGCTG
TATAGGGGAT AAATGAGATT GAATGGTGGC CACACTCAAA CCAACCAGGT CCTGTACATA
CAATGCATAT ACCAATTATA CCTACCAAAA AAAAAAAAAA AAAAAAAAAA AAAA (SEQ ID NO:18)

or a sequence homologous thereto encoding a polypeptide specific for xyloglucan with endoglucanase activity,

ii) is immunologically reactive with an antibody raised against a highly purified endoglucanase encoded by the DNA sequence defined in i) and derived from *Aspergillus aculeatus*, CBS 101.43, and is specific for xyloglucan.

More specifically, as used herein the term "specific for xyloglucan" means that the endoglucanse enzyme exhibits its highest endoglucanase activity on a xyloglucan substrate, and preferably less than 75% activity, more preferably less than 50% activity, most preferably less than about 25% activity, on other cellulose-containing substrates such as carboxymethyl cellulose, cellulose, or other glucans.

Preferably, the specificity of an endoglucanase towards xyloglucan is further defined as a relative activity determined as the release of reducing sugars at optimal conditions obtained by incubation of the enzyme with xyloglucan and the other substrate to be tested, respectively. For instance, the specificity may be defined as the xyloglucan to β-glucan activity (XGU/BGU), xyloglucan to carboxy methyl cellulose activity

(XGU/CMCU), or xyloglucan to acid swollen Avicell activity (XGU/AVIU), which is preferably greater than about 50, such as 75, 90 or 100.

The term "derived from" as used herein refers not only to an endoglucanase produced by strain CBS 101.43, but also an endoglucanase encoded by a DNA sequence isolated from strain CBS 101.43 and produced in a host organism transformed with said DNA sequence. The term "homologue" as used herein indicates a polypeptide encoded by DNA which hybridizes to the same probe as the DNA coding for an endoglucanase enzyme specific for xyloglucan under certain specified conditions (such as presoaking in 5xSSC and prehybridizing for 1 h at -40°C in a solution of 5xSSC, 5xDenhardt's solution, and 50 μg of denatured sonicated calf thymus DNA, followed by hybridization in the same solution supplemented with 50 μCi 32-P-dCTP labelled probe for 18 h at -40°C and washing three times in 2xSSC, 0.2% SDS at 40°C for 30 minutes). More specifically, the term is intended to refer to a DNA sequence which is at least 70% homologous to any of the sequences shown above encoding an endoglucanase specific for xyloglucan, including at least 75%, at least 80%, at least 85%, at least 90% or even at least 95% with any of the sequences shown above. The term is intended to include modifications of any of the DNA sequences shown above, such as nucleotide substitutions which do not give rise to another amino acid sequence of the polypeptide encoded by the sequence, but which correspond to the codon usage of the host organism into which a DNA construct comprising any of the DNA sequences is introduced or nucleotide substitutions which do give rise to a different amino acid sequence and therefore, possibly, a different amino acid sequence and therefore, possibly, a different protein structure which might give rise to an endoglucanase mutant with different properties than the native enzyme. Other examples of possible modifications are insertion of one or more nucleotides into the sequence, addition of one or more nucleotides at either end of the sequence, or deletion of one or more nucleotides at either end or within the sequence.

Endoglucanase specific for xyloglucan useful in the present invention preferably is one which has a XGU/BGU, XGU/CMU and/or XGU/AVIU ratio (as defined above) of more than 50, such as 75, 90 or 100.

Furthermore, the endoglucanase specific for xyloglucan is preferably substantially devoid of activity towards β-glucan and/or exhibits at the most 25% such as at the most 10% or about 5%, activity towards carboxymethyl cellulose and/or Avicell when the activity towards xyloglucan is 100%. In addition, endoglucanase specific for xyloglucan of the invention is preferably substantially devoid of transferase activity, an activity which has been observed for most endoglucanases specific for xyloglucan of plant origin.

Endoglucanase specific for xyloglucan may be obtained from the fungal species *A. aculeatus*, as described in WO 94/14953. Microbial endoglucanases specific for xyloglucan has also been described in WO 94/14953. Endoglucanases specific for xyloglucan from plants have

been described, but these enzymes have transferase activity and therefore must be considered inferior to microbial endoglucanses specific for xyloglucan whenever extensive degradation of xyloglucan is desirable. An additional advantage of a microbial enzyme is that it, in general, may be produced in higher amounts in a microbial host, than enzymes of other origins.

The xyloglucanase, when present, is incorporated into the treating compositions of the invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimize their performance efficiency in the laundry detergent and/or fabric care compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular laundry application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability.

Other suitable cleaning adjunct materials that can be added are enzyme oxidation scavengers. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials are also disclosed in WO 9307263 and WO 9307260 to Genencor International, WO 8908694, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, and in U.S. 4,507,219. Enzyme materials particularly useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868.

Various carbohydrase enzymes which impart antimicrobial activity may also be included in the present invention. Such enzymes include endoglycosidase, Type II endoglycosidase and glucosidase as disclosed in U.S. Patent Nos. 5,041,236, 5,395,541, 5,238,843 and 5,356,803 the disclosures of which are herein incorporated by reference. Of course, other enzymes having

antimicrobial activity may be employed as well including peroxidases, oxidases and various other enzymes.

It is also possible to include an enzyme stabilization system into the compositions of the present invention when any enzyme is present in the composition.

Perfumes - Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 2%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Non-limiting examples of perfume ingredients useful herein include: 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; ionone methyl; ionone gamma methyl; methyl cedrylone; methyl dihydrojasmonate; methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; para-hydroxy-phenyl-butanone; benzophenone; methyl beta-naphthyl ketone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; 7-hydroxy-3,7-dimethyl ocatanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecane; condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal and indol, condensation products of phenyl acetaldehyde and indol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; ethyl vanillin; heliotropin; hexyl cinnamic aldehyde; amyl cinnamic aldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; coumarin; decalactone gamma; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; beta-naphthol methyl ether; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; tricyclodecenyl propionate; tricyclodecenyl acetate; benzyl salicylate; cedryl acetate; and para-(tert-butyl) cyclohexyl acetate.

Particularly preferred perfume materials are those that provide the largest odor improvements in finished product compositions containing cellulases. These perfumes include but are not limited to: hexyl cinnamic aldehyde; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; benzyl salicylate; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; para-tert-butyl cyclohexyl acetate; methyl

dihydro jasmonate; beta-napthol methyl ether; methyl beta-naphthyl ketone; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gamma-2-benzopyrane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; anisaldehyde; coumarin; cedrol; vanillin; cyclopentadecanolide; tricyclodecenyl acetate; and tricyclodecenyl propionate.

Other perfume materials include essential oils, resinoids, and resins from a variety of sources including, but not limited to: Peru balsam, Olibanum resinoid, styrax, labdanum resin, nutmeg, cassia oil, benzoin resin, coriander and lavandin. Still other perfume chemicals include phenyl ethyl alcohol, terpineol, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)-cyclohexanol acetate, benzyl acetate, and eugenol. Carriers such as diethylphthalate can be used in the finished perfume compositions.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-tri-acetates, ethylenediamine tetrapro-prionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldi-glycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at lease low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder. Similarly, the so called "weak" builders such as citrate can also be used as chelating agents.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Composition pH

Dishwashing compositions of the invention will be subjected to acidic stresses created by food soils when put to use, i.e., diluted and applied to soiled dishes. If a composition with a pH greater than 7 is to be more effective, it preferably should contain a buffering agent capable of providing a generally more alkaline pH in the composition and in dilute solutions, i.e., about 0.1% to 0.4% by weight aqueous solution, of the composition. The pKa value of this buffering agent should be about 0.5 to 1.0 pH units below the desired pH value of the composition (determined as described above). Preferably, the pKa of the buffering agent should be from about 7 to about 10. Under these conditions the buffering agent most effectively controls the pH while using the least amount thereof.

The buffering agent may be an active detergent in its own right, or it may be a low molecular weight, organic or inorganic material that is used in this composition solely for maintaining an alkaline pH. Preferred buffering agents for compositions of this invention are nitrogen-containing materials. Some examples are amino acids such as lysine or lower alcohol amines like mono-, di-, and tri-ethanolamine. Other preferred nitrogen-containing buffering agents are Tri(hydroxymethyl)amino methane ($(HOCH_2)_3CNH_3$ (TRIS), 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl-propanol, 2-amino-2-methyl-1,3-propanol, disodium glutamate, N-methyl diethanolamide, 1,3-diamino-propanol N,N'-tetra-methyl-1,3-diamino-2-propanol, N,N-bis(2-hydroxyethyl)glycine (bicine) and N-tris (hydroxymethyl)methyl glycine (tricine). Mixtures of any of the above are also acceptable. Useful inorganic buffers/alkalinity sources include the alkali metal carbonates and alkali metal phosphates, e.g., sodium carbonate, sodium polyphosphate. For additional buffers see McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1997, McCutcheon Division, MC Publishing Company Kirk and WO 95/07971 both of which are incorporated herein by reference.

The buffering agent, if used, is present in the compositions of the invention herein at a level of from about 0.1% to 15%, preferably from about 1% to 10%, most preferably from about 2% to 8%, by weight of the composition.

Calcium and/or Magnesium Ions

The presence of calcium and/or magnesium (divalent) ions improves the cleaning of greasy soils for various compositions, i.e., compositions containing alkyl ethoxy sulfates and/or

polyhydroxy fatty acid amides. This is especially true when the compositions are used in softened water that contains few divalent ions. It is believed that calcium and/or magnesium ions increase the packing of the surfactants at the oil/water interface, thereby reducing interfacial tension and improving grease cleaning.

Compositions of the invention herein containing magnesium and/or calcium ions exhibit good grease removal, manifest mildness to the skin, and provide good storage stability. These ions can be present in the compositions herein at an active level of from about 0.1% to 4%, preferably from about 0.3% to 3.5%, more preferably from about 0.5% to 1%, by weight.

Preferably, the magnesium or calcium ions are added as a hydroxide, chloride, acetate, formate, oxide or nitrate salt to the compositions of the present invention. Calcium ions may also be added as salts of the hydrotrope.

The amount of calcium or magnesium ions present in compositions of the invention will be dependent upon the amount of total surfactant present therein. When calcium ions are present in the compositions of this invention, the molar ratio of calcium ions to total anionic surfactant should be from about 0.25:1 to about 2:1.

Formulating such divalent ion-containing compositions in alkaline pH matrices may be difficult due to the incompatibility of the divalent ions, particularly magnesium, with hydroxide ions. When both divalent ions and alkaline pH are combined with the surfactant mixture of this invention, grease cleaning is achieved that is superior to that obtained by either alkaline pH or divalent ions alone. Yet, during storage, the stability of these compositions becomes poor due to the formation of hydroxide precipitates. Therefore, chelating agents discussed hereinbefore may also be necessary.

Other Ingredients - The detergent compositions will further preferably comprise one or more detersive adjuncts selected from the following: soil release polymers, polymeric dispersants, polysaccharides, abrasives, bactericides, tarnish inhibitors, builders, enzymes, opacifiers, dyes, buffers, antifungal or mildew control agents, insect repellents, perfumes, hydrotropes, thickeners, processing aids, suds boosters, brighteners, anti-corrosive aids, stabilizers antioxidants and chelants. A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, antioxidants, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C_{10}-C_{16} alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C_{10}-C_{14} monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous.

An antioxidant can be optionally added to the detergent compositions of the present invention. They can be any conventional antioxidant used in detergent compositions, such as 2,6-di-tert-butyl-4-methylphenol (BHT), carbamate, ascorbate. thiosulfate, monoethanolamine(MEA), diethanolamine, triethanolamine. etc. It is preferred that the antioxidant, when present, be present in the composition from about 0.001% to about 5% by weight.

Various detersive ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the detersive ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detersive ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detersive function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C_{13-15} ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches. bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents. including liquid laundry detergent compositions.

Further , these hand dishwashing detergent embodiments preferably further comprises a hydrotrope. Suitable hydrotropes include sodium, potassium, ammonium or water-soluble substituted ammonium salts of toluene sulfonic acid, naphthalene sulfonic acid, cumene sulfonic acid, xylene sulfonic acid.

The detergent compositions of this invention can be in any form, including granular, paste, gel or liquid. Highly preferred embodiments are in liquid or gel form. Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

An example of the procedure for making granules of the detergent compositions herein is as follows: - Linear aklylbenzenesulfonate, citric acid, sodium silicate, sodium sulfate perfume, diamine and water are added to, heated and mixed via a crutcher. The resulting slurry is spray dried into a granular form.

An example of the procedure for making liquid detergent compositions herein is as follows: - To the free water and citrate are added and dissolved. To this solution amine oxide, betaine, ethanol, hydrotrope and nonionic surfactant are added. If free water isn't available, the citrate are added to the above mix then stirred until dissolved. At this point, an acid is added to neutralize the formulation. It is preferred that the acid be chosen from organic acids such as maleic and citric, however, inorganic mineral acids may be employed as well. In preferred embodiments these acids are added to the formulation followed by diamine addition. AExS is added last.

Non-Aqueous Liquid Detergents

The manufacture of liquid detergent compositions which comprise a non-aqueous carrier medium can be prepared according to the disclosures of U.S. Patents 4,753,570; 4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such compositions can contain various particulate detersive ingredients stably suspended therein. Such non-aqueous compositions thus comprise a LIQUID PHASE and, optionally but preferably, a SOLID PHASE, all as described in more detail hereinafter and in the cited references.

The compositions of this invention can be used to form aqueous washing solutions for use hand dishwashing. Generally, an effective amount of such compositions is added to water to form such aqueous cleaning or soaking solutions. The aqueous solution so formed is then contacted with the dishware, tableware, and cooking utensils.

An effective amount of the detergent compositions herein added to water to form aqueous cleaning solutions can comprise amounts sufficient to form from about 500 to 20,000 ppm of composition in aqueous solution. More preferably, from about 800 to 5,000 ppm of the detergent compositions herein will be provided in aqueous cleaning liquor.

METHOD OF USE

The present invention also relates to a method for providing increased suds volume and increased suds retention while hand washing dishware or cookware articles in need of cleaning, comprising the step of contacting said articles with an aqueous solution of a detergent composition suitable for use in hand dishwashing, said composition comprising:

a) an effective amount of a polymeric suds stabilizer as hereinbefore defined;

b) an effective amount of a detersive surfactant; and

c) the balance carriers and other adjunct ingredients;

provided the pH of a 10% aqueous solution of said composition is from about 4 to about 12.

The present invention also relates to a means for preventing the redeposition of grease, oils, and dirt, especially grease, from the hand washing solution onto dishware. This method comprises contacting an aqueous solution of the compositions of the present invention with soiled dishware and washing said dishware with said aqueous solution.

An effective amount of the detergent compositions herein added to water to form aqueous cleaning solutions according to the method of the present invention comprises amounts sufficient to form from about 500 to 20,000 ppm of composition in aqueous solution. More preferably, from about 800 to 2,500 ppm of the detergent compositions herein will be provided in aqueous cleaning liquor.

The liquid detergent compositions of the present invention are effective for preventing the redeposition of grease from the wash solution back onto the dishware during washing. One measure of effectiveness of the compositions of the present invention involves redeposition tests. The following test and others of similar nature are used to evaluate the suitability of the formulas described herein.

A polyethylene 2 L graduated cylinder is filled to the 1 L graduation mark with an aqueous (water = 7 grain) solution comprising from about 500 to about 20,000 ppm of a liquid detergent composition according to the present invention. A synthetic greasy soil composition is then added to the cylinder and the solution is agitated. After a period of time the solution is decanted from the graduated cylinder and the interior walls of the graduated cylinder are rinsed with a suitable solvent or combination of solvents to recover any re-deposited greasy soil. The solvent is removed and the weight of greasy soil which remains in solution is determined by subtracting the amount of soil recovered from the amount initially added to the aqueous solution.

Other re-deposition test include immersion of tableware, flatware, and the like and recovering any re-deposited soil.

The above test can be further modified to determine the increased amount of suds volume and suds duration. The solution is first agitated then subsequently challenged with portions of greasy soil with agitation between each subsequent soil addition. The suds volume can be easily determined by using the vacant volume of the 2 L cylinder as a guide.

EXAMPLE 1

Preparation of Poly(HEA-*co*-DMAM-*co*-AA) (9:3:1) Terpolymer

2-Hydroxyethyl acrylate (25.00 g, 215.3 mmol), 2-(dimethylamino)ethyl methacrylate (11.28 g, 71.8 mmol), acrylic acid (1.71 g, 23.7 mmol), 2,2'-azobisisobutyronitrile (0.26 g, 1.6 mmol), 1,4-dioxane (150 ml) and 2-propanol (30 ml) are placed into a 500 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet. The mixture is sparged with nitrogen for 30 minutes to remove dissolved oxygen. The mixture is heated for 18 hours with stirring at 65°C. TLC (diethyl ether) indicates consumption of

monomer. An equal volume of water is added and the mixture is concentrated under vacuum by rotary evaporation to remove the solvent. Water is added to make a 10% solution and the mixture is lyophilized and then pulverized in a blender to yield an off-white powder. NMR is consistent with the desired compound.

EXAMPLE 2

Preparation of Poly(HPA-*co*-DMAM-*co*-AA) (9:3:1) Terpolymer

Hydroxypropyl acrylate (25.00 g, 192.1 mmol), 2-(dimethylamino)ethyl methacrylate (10.07 g, 64.0 mmol), acrylic acid (1.52 g, 21.1 mmol), 2,2'-azobisisobutyronitrile (0.23 g, 1.4 mmol), 1,4-dioxane (150 ml) and 2-propanol (30 ml) are placed into a 500 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet. The mixture is sparged with nitrogen for 30 minutes to remove dissolved oxygen. The mixture is heated for 18 hours with stirring at 65°C. TLC (diethyl ether) indicates consumption of monomer. An equal volume of water is added and the mixture is concentrated under vacuum by rotary evaporation to remove the solvent. Water is added to make a 10% solution and the mixture is lyophilized and then pulverized in a blender to yield an off-white powder. NMR is consistent with the desired compound.

EXAMPLE 3

Preparation of Poly(HEA-*co*-DMAM) (3:1) Copolymer

2-Hydroxyethyl acrylate (30.00 g, 258.4 mmol), 2-(dimethylamino)ethyl methacrylat (13.54 g, 86.1 mmol), 2,2'-azobisisobutyronitrile (0.28 g, 1.7 mmol), 1,4-dioxane (150 ml) and 2-propanol (30 ml) are placed into a 500 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet. The mixture is sparged with nitrogen for 30 minutes to remove dissolved oxygen. The mixture is heated for 18 hours with stirring at 65°C. TLC (diethyl ether) indicates consumption of monomer. An equal volum of water is added and the mixture is concentrated under vacuum by rotary evaporation to remove the solvent. Water is added to make a 10% solution and the mixture is lyophilized and then pulverized in a blender to yield an off-white powder. NMR is consistent with the desired compound.

Example 3.1

Preparation of Poly(HEA-*co*-DMAM) (3:1) Copolymer

DMAEMA copolymer was prepared from DMAEMA (also known as DMAM), citric acid, water, and HEA alone or with AA. In particular, the HEA:DMAEMA copolymer was made with two separate monomer feeds. DMAEMA was neutralized by adding it to citric acid and water. HEA was mixed with water. The two monomer mixtures, i.e., DMAEMA (neutralized with citric acid) and HEA, and the redox initiator components, namely sodium persulfate solution and sodium metabisulfite solution were metered separately but simultaneously over 2.5 hours at

85°C to a reaction vessel. Then the combined ingredients were held for 1 hour and extra initiator was added to further reduce residual monomer. Then the combined ingredients were held for another hour. The reaction temperature was 85°C and there was 27.0% active polymer.

The residual monomer values were measured with HPLC (high pressure liquid chromatography) at room temperature and measured after heating at 80°C in a phosphate buffer (pH = 4.2) for several hours. The sample after heating at 80°C would reveal the amount of monomer that was not polymerized but bound to the polymer.

The polymer concentration of the analyzed samples was 1-5 mg/ml active polymer. In the following Table, % initiator is based on weight percent of the monomers. All residual monomer values are parts per million based on active content (polymer solids).

The presence of AA listed in Table 1 was most likely due to the acrylic acid present in the HEA (<1%) raw material as supplied or to a small extent may be due to some hydrolysis of HEA.

The residual monomer values were as shown in TABLE A. All residual monomer values are parts per million based on active content (polymer solids).

Further treatment with extra amount of initiator in this example was able to reduce the residual monomer to <500 ppm (when heated at 80°C for 4 hours).

In the Table A of this Example under the headings "Residual Monomer Before Further Treatment : room temp (80°C/4 hrs)" and "Residual Monomer After Further Treatment : room temp (80°C/4 hrs)", the values outside of parentheses are those in ppm based on active polymer measured at room temperature before heating and the values in parentheses are those in ppm based on active polymer of the analyzed samples after heating to 80°C for four hours.

The results of these samples were in TABLES A and B. In the tables ND means non-detectable (less than 2 ppm).

TABLE A - Results of Citric Acid Neutralized HEA:DMAEMA (3:1) Copolymer Prepared With Separate Monomer Feeds

Initiator	Monomer pH	Residual Monomer Before Further Treatment : room temp (80°C /4hrs)	Residual Monomer After Further Treatment : room temp (80°C /4hrs)
1) 2.1% $Na_2S_2O_8$ 2) 0.6% $Na_2S_2O_5$	DMAEMA= 5.2 HEA=3.3	HEA= 6 (309) DMAEMA= 5 (18) AA= 92 (1630) MAA= ND (ND)	HEA= 8(83) DMAEMA= 8 (ND) AA= 27 (119) MAA= ND (ND)

TABLE B - Results of Citric Acid Neutralized HEA:DMAEMA (3:1) Copolymer Prepared With Separate Monomer Feeds

% SOLID (Theoretical Value)	B.V. (As is, 25°C)	pH (as is, 25°C)	Appearance
32.95%	1070 cps (#31v, 60 rpm)	3.95	Clear yellow solution

EXAMPLE 4

Preparation of Poly(HEA-*co*-DMAM-*co*-AA) (3:9:1) Terpolymer

2-Hydroxyethyl acrylate (5.00 g, 43.1 mmol), 2-(dimethylamino)ethyl methacrylate (20.31 g, 129.2 mmol), acrylic acid (1.02 g, 14.2 mmol), 2,2'-azobisisobutyronitrile (0.16 g, 1.0 mmol), 1,4-dioxane (92 ml) and 2-propanol (18 ml) are placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet. The mixture is sparged with nitrogen for 30 minutes to remove dissolved oxygen. The mixture is heated for 18 hours with stirring at 65°C. TLC (diethyl ether) indicates consumption of monomer. An equal volume of water is added and the mixture is concentrated under vacuum by rotary evaporation to remove the solvent. Water is added to make a 10% solution and the mixture is lyophilized and then pulverized in a blender to yield an off-white powder. NMR is consistent with the desired compound.

EXAMPLE 5

Preparation of Poly(PEG acrylate-*co*-DMAM-*co*-AA) (9:3:1) Terpolymer

Poly(ethylene glycol) acrylate (20.00 g, 41.1 mmol), 2-(dimethylamino)ethyl methacrylate (2.15 g, 13.7 mmol), acrylic acid (0.33 g, 4.5 mmol), 2,2'-azobisisobutyronitrile (0.001 g, 0.3 mmol), 1,4-dioxane (79 ml) and 2-propanol (16 ml) are placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet. The mixture is sparged with nitrogen for 30 minutes to remove dissolved oxygen. The mixture is heated for 18 hours with stirring at 65°C. TLC (diethyl ether) indicates consumption of monomer. An equal volume of water is added and the mixture is concentrated under vacuum by rotary evaporation to remove the solvent. Water is added to make a 10% solution and the mixture is lyophilized to yield a viscous yellow oil. Water is added to make a 10% solution. NMR is consistent with the desired compound.

EXAMPLE 6

Preparation of Poly(DMAM-*co*-butylvinylether) (1:1) Copolymer

2-(Dimethylamino)ethyl methacrylate (8.00 g, 50.9 mmol), *N*-butylvinylether (5.10 g, 50.9 mmol), 2,2'-azobisisobutyronitrile (0.08 g, 0.5 mmol), 1,4-dioxane (75 ml) and 2-propanol

(15 ml) are placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet. The mixture is sparged with nitrogen for 30 minutes to remove dissolved oxygen. The mixture is heated for 18 hours with stirring at 65°C. TLC (diethyl ether) indicates consumption of monomer. An equal volume of *t*-butanol is added and the mixture is concentrated under vacuum by rotary evaporation to remove the solvent. *t*-Butanol is added to make a 10% solution and the mixture is lyophilized to yield waxy solid. NMR is consistent with the desired compound.

Example 7

Preparation of Poly(2-diethylaminoethyl vinyl ether-co-ethyleneglycol monovinyl ether)

Aluminum chloride (1.0 g, 7.5 mmol) is added to a flask containing benzene (200 mL). A mixture of 2-diethylaminoethyl vinyl ether (100.24 g, 0.70 mol) and ethyleneglycol monovinyl ether (183.25g, 2.08 mol) is added gradually so as to keep the reaction mixture at 60°-80°C. After addition is complete, the reaction mixture is heated for 3 h. The solvent is removed by rotary evaporation at room temperature and then stripped by kugelrohr distillation at 60 °C (0.5 mm Hg) for 2 h to yield the polymer.

The following are non-limiting examples of liquid detergent compositions comprising the polymeric suds extenders according to the present invention.

TABLE I

	weight %		
Ingredients	**8**	**9**	**10**
C_{12}-C_{15} Alkyl sulphate	--	28.0	25.0
C_{12}-C_{13} Alkyl ($E_{0.6-3}$) sulfate	30	--	--
C_{12} Amine oxide	5.0	3.0	7.0
C_{12}-C_{14} Betaine	3.0	--	1.0
C_{12}-C_{14} Polyhydroxy fatty acid amide	--	1.5	--
C_{10} Alcohol Ethoxylate E_9 [1]	2.0	--	4.0
Diamine [2]	1.0	--	7.0
Mg^{2+} (as $MgCl_2$)	0.25	--	--
Citrate (cit2K3)	0.25	--	--
Polymeric suds booster [3]	1.25	2.6	0.9
Minors and water [4]	balance	balance	balance
pH of a 10% aqueous solution	9	10	10

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. 1,3-diaminopentane sold as Dytek EP.
3. Suds Booster according to the present invention, preferably a suds booster in accordance with Examples 1-7, more preferably poly(HEA-*co*-DMAM-*co*-AA) (9:3:1) Terpolymer of Example 1.
4. Includes perfumes, dyes, ethanol, etc.

TABLE II

weight %

Ingredients	11	12	13
C_{12}-C_{13} Alkyl ($E_{0.6-3}$) sulfate	--	15.0	10.0
Paraffin sulfonate	20.0	--	--
Na C_{12}-C_{13} linear alkylbenzene sulfonate	5.0	15.0	12.0
C_{12}-C_{14} Betaine	3.0	1.0	--
C_{12}-C_{14} Polyhydroxy fatty acid amide	3.0	--	1.0
C_{10} Alcohol Ethoxylate E_9 [1]	--	--	20.0
Diamine [2]	1.0	-	7.0
DTPA [3]	--	0.2	--
Mg^{2+} (as $MgCl_2$)	1.0	--	--
Ca^{2+} (as Ca(citrate)$_2$)	--	0.5	--
Protease [4]	0.01	--	0.001
Amylase [5]	--	0.001	0.001
Hydrotrope [6]	2.0	1.5	3.0
Polymeric suds booster [7]	0.5	3.0	0.5
Minors and water [8]	balance	balance	balance
pH of a 10% aqueous solution	9.3	8.5	11

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. 1,3-bis(methylamino)cyclohexane.
3. Diethylenetriaminepentaacetate.
4. Suitable protease enzymes include Savinase®; Maxatase®; Maxacal®; Maxapem 15®; subtilisin BPN and BPN'; Protease B; Protease A; Protease D; Primase®; Durazym®; Opticlean®;and Optimase®; and Alcalase®.

5. Suitable amylase enzymes include Termamyl®, Fungamyl®; Duramyl®; BAN®, and the amylases as described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK/96/00056.
6. Suitable hydrotropes include sodium, potassium, ammonium or water-soluble substituted ammonium salts of toluene sulfonic acid, naphthalene sulfonic acid, cumene sulfonic acid, xylene sulfonic acid.
7. Suds Booster according to the present invention, preferably a suds booster in accordance with Examples 1-7, more preferably poly(HPA-*co*-DMAM-*co*-AA) (9:3:1) Terpolymer of Example 2.
8. Includes perfumes, dyes, ethanol, etc.

TABLE III

	weight %			
Ingredients	**14**	**15**	**16**	**17**
C_{12}-C_{15} Alkyl (E_1) sulfate	--	30.0	--	--
C_{12}-C_{15} Alkyl ($E_{1.4}$) sulfate	30.0	--	27.0	--
C_{12}-C_{15} Alkyl ($E_{2.2}$) sulfate	--	--	--	15
C_{12} Amine oxide	5.0	5.0	5.0	3.0
C_{12}-C_{14} Betaine	3.0	3.0	--	--
C_{10} Alcohol Ethoxylate E_9 [1]	2.0	2.0	2.0	2.0
Diamine [2]	1.0	2.0	4.0	2.0
Mg^{2+} (as $MgCl_2$)	0.25	0.25	--	--
Ca^{2+} (as $Ca(citrate)_2$)	--	0.4	--	--
Polymeric suds booster [3]	0.5	1.0	0.75	5.0
Minors and water [4]	balance	balance	balance	balance
pH of a 10% aqueous solution	7.4	7.6	7.4	7.8

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. 1,3-diaminopentane sold as Dytek EP.
3. Suds Booster according to the present invention, preferably a suds booster in accordance with Examples 1-7, more preferably poly(HEA-*co*-DMAM) (3:1) Copolymer of Example 3.
4. Includes perfumes, dyes, ethanol, etc.

TABLE IV

	weight %		
Ingredients	**18**	**19**	**20**

C_{12}-C_{13} Alkyl ($E_{0.6-3}$) sulfate	–	15.0	10.0
Paraffin sulfonate	20.0	--	–
Na C_{12}-C_{13} linear alkylbenzene sulfonate	5.0	15.0	12.0
C_{12}-C_{14} Betaine	3.0	1.0	–
C_{12}-C_{14} Polyhydroxy fatty acid amide	3.0	–	1.0
C_{10} Alcohol Ethoxylate E_9 [1]	–	--	20.0
Diamine [2]	1.0	--	7.0
Mg^{2+} (as $MgCl_2$)	1.0	--	–
Ca^{2+} (as $Ca(citrate)_2$)	–	0.5	–
Protease [3]	0.1	--	--
Amylase [4]	–	0.02	–
Lipase [5]	–	--	0.025
DTPA [6]	–	0.3	--
Citrate (cit2K3)	0.65	--	–
Polymeric suds booster [7]	1.5	2.2	3.0
Minors and water [8]	balance	balance	balance
pH of a 10% aqueous solution	9.3	8.5	11

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. 1,3-bis(methylamino)cyclohexane.
3. Suitable protease enzymes include Savinase®; Maxatase®; Maxacal®; Maxapem 15®; subtilisin BPN and BPN'; Protease B; Protease A; Protease D; Primase®; Durazym®; Opticlean®;and Optimase®; and Alcalase ®.
4. Suitable amylase enzymes include Termamyl®, Fungamyl®; Duramyl®; BAN®, and the amylases as described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK/96/00056.
5. Suitable lipase enzymes include Amano-P; M1 Lipase®; Lipomax®; Lipolase®; D96L - lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Patent Application Serial No. 08/341,826; and the *Humicola lanuginosa* strain DSM 4106
6. Diethylenetriaminepentaacetate.
7. Suds Booster according to the present invention, preferably a suds booster in accordance with Examples 1-7, more preferably poly(HEA-*co*-DMAM-*co*-AA) (3:9:1) Terpolymer of Example 4.
8. Includes perfumes, dyes, ethanol, etc.

TABLE V

Ingredients	21 (weight %)	22 (weight %)	23 (weight %)
C_{12}-C_{13} Alkyl ($E_{0.6-3}$) sulfate	--	27.0	--
C_{12}-C_{14} Betaine	2.0	2.0	--
C_{14} Amine oxide	2.0	5.0	7.0
C_{12}-C_{14} Polyhydroxy fatty acid amide	2.0	--	--
C_{10} Alcohol Ethoxylate E_9 [1]	1.0	--	2.0
Hydrotrope	--	--	5.0
Diamine [2]	4.0	2.0	5.0
Ca^{2+} (as $Ca(citrate)_2$)	--	0.1	0.1
Protease [3]	--	0.06	0.1
Amylase [4]	0.005	--	0.001
Lipase [5]	--	0.001	--
DTPA [6]	--	0.1	0.1
Citrate (cit2K3)	0.3	--	--
Polymeric suds booster [7]	0.5	0.8	2.5
Minors and water [8]	balance	balance	balance
pH of a 10% aqueous solution	10	9	9.2

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. 1,3-diaminopentane sold as Dytek EP.
3. Suitable protease enzymes include Savinase®; Maxatase®; Maxacal®; Maxapem 15®; subtilisin BPN and BPN'; Protease B; Protease A; Protease D; Primase®; Durazym®; Opticlean®;and Optimase®; and Alcalase ®.
4. Suitable amylase enzymes include Termamyl®, Fungamyl®; Duramyl®; BAN®, and the amylases as described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK/96/00056.
5. Suitable lipase enzymes include Amano-P; M1 Lipase®; Lipomax®; Lipolase®; D96L - lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in US Patent Application Serial No. 08/341,826; and the *Humicola lanuginosa* strain DSM 4106
6. Diethylenetriaminepentaacetate.
7. Suds Booster according to the present invention, preferably a suds booster in accordance with Examples 1-7, more preferably poly(PEG acrylate-*co*-DMAM-*co*-AA) (9:3:1) Terpolymer of Example 5.

8. Includes perfumes, dyes, ethanol, etc.

TABLE VI

weight %

Ingredients	24	25	26
C_{12}-C_{13} Alkyl ($E_{1.4}$) sulfate	33.29	24.0	--
C_{12}-C_{13} Alkyl ($E_{0.6}$) sulfate	--	--	26.26
C_{12}-C_{14} Polyhydroxy fatty acid amide	4.2	3.0	1.37
C_{14} Amine oxide	4.8	2.0	1.73
C_{11} Alcohol Ethoxylate E_9 [1]	1.0	4.0	4.56
C_{12}-C_{14} Betaine	--	2.0	1.73
$MgCl_2$	0.72	0.47	0.46
Calcium citrate	0.35	--	--
Polymeric suds booster [2]	0.5	1.0	2.0
Minors and water [3]	balance	balance	balance
pH of a 10% aqueous solution	7.4	7.8	7.8

1. E_9 Ethoxylated Alcohols as sold by the Shell Oil Co.
2. Suds Booster according to the present invention, preferably a suds booster in accordance with Examples 1-7, more preferably poly(DMAM-*co*-butylvinylether) (1:1) Copolymer of Example 6.
3. Includes perfumes, dyes, ethanol, etc.

Table VII

	27	28	29	30	31
AE0.6S[1]	28.80	28.80	26.09	26.09	26.09
Amine oxide[2]	7.20	7.20	6.50	6.50	6.50
Citric acid	3.00	----	----	----	----
Maleic acid	----	2.50	----	----	----
Suds boosting polymer[3]	0.22	0.22	0.20	0.20	0.20
Sodium Cumene Sulfonate	3.30	3.30	3.50	3.50	3.50
Ethanol 40B	6.50	6.50	6.50	6.50	6.50
C10E8	----	----	3.00	3.00	3.00
C11E9[4]	3.33	3.33	----	----	----
Diamine[5]	0.55	0.55	0.50	0.50	0.50
Perfume	0.31	0.31	----	----	----
Water	BAL.	BAL.	BAL.	BAL.	BAL.

Viscosity (cps @ 70F)	330	330	150	330	650
pH @ 10%	9.0	9.0	8.3	9.0	9.0

1. C12-13 alkyl ethoxy sulfonate containing an average of 0.6 ethoxy groups.

2. C_{12}-C_{14} Amine oxide.

3 Suds Booster according to the present invention, preferably a suds booster in accordance with Examples 1-7, more preferably poly(2-diethylaminoethyl vinyl ether-co-ethyleneglycol monovinyl ether) of Example 7.

4. C11 Alkyl ethoxylated surfactant containing 9 ethoxy groups.

5. 1,3 bis(methylamine)-cyclohexane.

6. C10 Alkyl ethoxylated surfactant containing 8 ethoxy groups.

7. 1,3 pentane diamine.

Table VIII

	32	33	34	35	36
AE0.6S[1]	26	26	26	26	26
Amine oxide[2]	6.5	6.5	7.5	7.5	7.5
Citric acid	3.0	-	2.5	-	3.0
Maleic acid	-	2.5	-	3.0	-
C10E8[6]	3	3	4.5	4.5	4.5
Diamine[5]	0.5	0.5	1.25	0	1.25
Diamine[7]	0	0	0	1	
Suds boosting polymer[3]	0	0.2	0.5	0.5	0.5
Sodium cumene sulphonate	3.5	3.5	2	2	2
Ethanol	8	8	8	8	8
pH	9	9	9	8	10

1. C12-13 alkyl ethoxy sulfonate containing an average of 0.6 ethoxy groups.

2. C_{12}-C_{14} Amine oxide.

3. Suds Booster according to the present invention, preferably a suds booster in accordance with Examples 1-7, more preferably poly(HEA-*co*-DMAM-*co*-AA) (3:9:1) Terpolymer of Example 4.

4. C11 Alkyl ethoxylated surfactant containing 9 ethoxy groups.

5. 1,3 bis(methylamine)-cyclohexane.

6. C10 Alkyl ethoxylated surfactant containing 8 ethoxy groups.

7. 1,3 pentane diamine.

WHAT IS CLAIMED IS:

1. A liquid detergent composition having increased suds volume and suds retention suitable for use in hand dishwashing, said compositions comprising:

a) an effective amount of a polymeric suds stabilizer, said stabilizer comprising:

i) units capable of having a cationic charge at a pH of from about 4 to about 12; provided that said suds stabilizer has an average cationic charge density of 2.77 or less units per 100 daltons molecular weight at a pH of from about 4 to about 12;

b) an effective amount of a detersive surfactant; and

c) the balance carriers and other adjunct ingredients;

provided that a 10% aqueous solution of said detergent composition has a pH of from about 4 to about 12.

2. The composition according to Claim 1 wherein said polymeric suds stabilizer (a) further comprises:

ii) one or more units having one or more hydroxyl groups, provided that said suds stabilizer has a hydroxyl group density of 0.5 or less.

3. The composition according to Claim 1 wherein said polymeric suds stabilizer (a) further comprises:

iii) one or more units having one or more hydrophobic groups selected from the group consisting of non-hydroxyl groups, non-cationic groups, non-anionic groups, non-carbonyl groups, and/or non-H-bonding groups.

4. The composition according to Claim 1 wherein said polymeric suds stabilizer has an average cationic charge density of from about 0.01 to about 2.75 units per 100 daltons molecular weight at a pH of from about 4 to about 12.

5. The composition according to Claim 4 wherein said polymeric suds stabilizer has an average cationic charge density of from about 0.1 to about 2.75 units per 100 daltons molecular weight at a pH of from about 4 to about 12.

6. The composition according to Claim 5 wherein said polymeric suds stabilizer has an average cationic charge density of from about 0.75 to about 2.25 units per 100 daltons molecular weight at a pH of from about 4 to about 12.

7. The composition according to Claim 2 wherein said polymeric suds stabilizer has a hydroxyl group density of from about 0.0001 to about 0.4.

8. The composition according to Claim 1 wherein said polymeric suds stabilizer (a) further comprises a hydrophilic group-containing unit.

9. The composition according to Claim 1 wherein said polymeric suds stabilizer (a) further comprises an anionic unit.

10. The composition according to Claim 1 wherein said polymeric suds stabilizer (a) further comprises:

iv) units capable of having an anionic charge at a pH of from about 4 to about 12;

v) units capable of having an anionic charge and a cationic charge at a pH of from about 4 to about 12;

vi) units having no charge at a pH of from about 4 to about 12; and

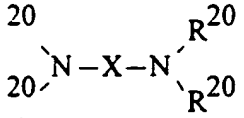
vii) mixtures of units (iv), (v), (vi), and (vii).

11. The composition according to Claim 1 wherein said polymeric suds stabilizer has an average molecular weight of from about 1,000 to about 2,000,000 daltons.

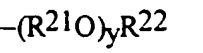
12. The composition according to Claim 1 further comprising from about 0.25% to about 15% of a diamine having molecular weight less than or equal to 400 g/mol.

13. The composition according to Claim 12 wherein said diamine is 1,3-bis(methylamine)-cyclohexane.

14. The composition according to Claim 12 wherein said diamine has the formula:

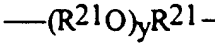


wherein each R^{20} is independently selected from the group consisting of hydrogen, C_1-C_4 linear or branched alkyl, alkyleneoxy having the formula:



wherein R^{21} is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^{22} is hydrogen, C_1-C_4 alkyl, and mixtures thereof; y is from 1 to about 10; X is a unit selected from:

i) C_3-C_{10} linear alkylene, C_3-C_{10} branched alkylene, C_3-C_{10} cyclic alkylene, C_3-C_{10} branched cyclic alkylene, an alkyleneoxyalkylene having the formula:



wherein R^{21} and y are the same as defined herein above;

ii) C_3-C_{10} linear, C_3-C_{10} branched linear, C_3-C_{10} cyclic, C_3-C_{10} branched cyclic alkylene, C_6-C_{10} arylene, wherein said unit comprises one or more electron donating or electron withdrawing moieties which provide said diamine with a pK_a greater than about 8; and

iii) mixtures of (i) and (ii)

provided said diamine has a pK_a of at least about 8.

15. The composition according to Claim 14 wherein each R^{20} is hydrogen and X is C_3-C_6 linear alkylene, C_3-C_6 branched alkylene, and mixtures thereof.

16. The composition according to Claim 1 wherein the detersive surfactant (b) is selected from the group consisting of linear alkyl benzene sulfonates, α-olefin sulfonates, paraffin sulfonates, methyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfates, alkyl sulfonates, alkyl alkoxy carboxylates, alkyl alkoxylated sulfates, sarcosinates, taurinates, and mixtures thereof.

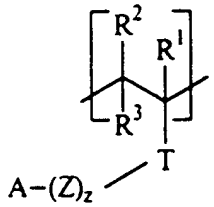
17. The composition according to Claim 1, wherein said other adjuncts ingredients (c) is selected from the group consisting of : soil release polymers, polymeric dispersants, polysaccharides, abrasives, bactericides, tarnish inhibitors, builders, enzymes, opacifiers, dyes, perfumes, thickeners, antioxidants, processing aids, suds boosters, buffers, antifungal or mildew control agents, insect repellants, anti-corrosive aids, chelants and mixtures thereof.

18. The composition according to Claim 1, wherein said detersive surfactant (b) is selected from the group consisting of amine oxides, polyhydroxy fatty acid amides, betaines, sulfobetaines, alkyl polyglycosides, alkyl ethoxylates, and mixtures thereof.

19. The composition according to Claim 1, wherein said polymeric suds stabilizer (a) is a proteinaceous suds stabilizer.

20. The composition according to Claim 1, further comprising an enzyme selected from the group consisting of protease, amylase, and mixtures thereof.

21. The composition according to Claim 1, wherein said polymeric suds stabilizer comprises a cationic unit of the formula:



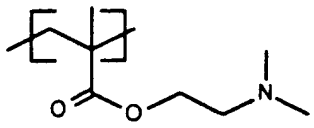
[I]

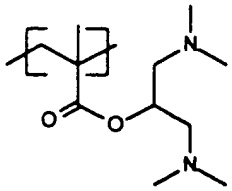
wherein each of R^1, R^2 and R^3 are independently selected from the group consisting of hydrogen, C_1 to C_6 alkyl, and mixtures thereof; T is selected from the group consisting of substituted or unsubstituted, saturated or unsaturated, linear or branched radicals selected from the group consisting of alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, ester, ether, carbonyl, amido, amino, glycidyl, carbanato, carbamate, carboxylic, and carboalkoxy radicals and mixtures thereof; Z is selected from the group consisting of: -(CH_2)-, $(CH_2$-CH=CH)-, -$(CH_2$-CHOH)-, $(CH_2$-CHNR^4)-, -$(CH_2$-CHR^5-O)- and mixtures thereof; R^4 and R^5 are selected from the group consisting of hydrogen, C_1 to C_6 alkyl and mixtures thereof; z is an integer selected from about 0 to about 12; A is NR^6R^7 or $NR^6R^7R^8$ wherein each of R^6, R^7 and R^8, when present, are independently selected from the group consisting of H, C_1-C_8 linear or branched alkyl, alkyleneoxy having the formula:

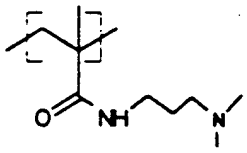
$$—(R^9O)_yR^{10}$$

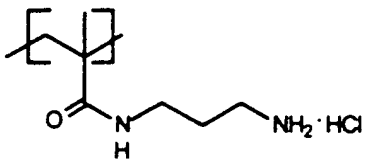
wherein R^9 is C_2-C_4 linear or branched alkylene, and mixtures thereof; R^{10} is hydrogen, C_1-C_4 alkyl, and mixtures thereof; and y is from 1 to about 10.

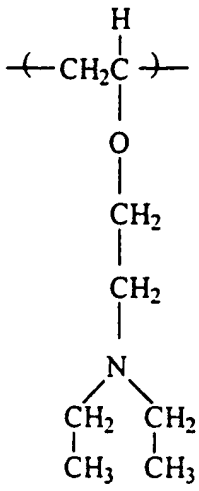
22. The composition according to Claim 21, wherein said polymeric suds stabilizer (a) comprises a cationic unit of the formula selected from the group consisting of:

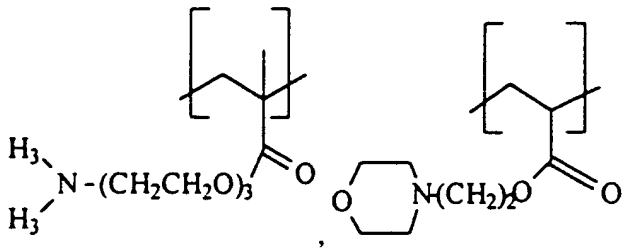


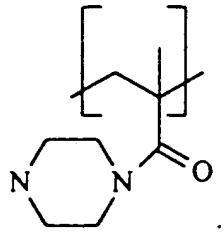












23. A method for providing extended suds volume and suds duration when dishware in need of cleaning is washed, comprising the step of contacting said dishware with an aqueous solution of a liquid detergent comprising:

a) an effective amount of a polymeric suds stabilizer, said stabilizer comprising:

i) units capable of having a cationic charge at a pH of from about 4 to about 12;

provided that said suds stabilizer has an average cationic charge density of 2.77 or less units per 100 daltons molecular weight at a pH of from about 4 to about 12;

b) an effective amount of a detersive surfactant; and

c) the balance carriers and other adjunct ingredients;

provided that a 10% aqueous solution of said detergent composition has a pH of from about 4 to about 12.

5

ABSTRACT

The present invention relates to liquid detergent compositions comprising a polymeric material which is a suds enhancer and a suds volume extender, said compositions having increased effectiveness for preventing re-deposition of grease during hand washing. The polymeric material which are suitable as suds volume and suds endurance enhancers comprise an effective amount of a polymeric suds stabilizer comprise:

i) units capable of having a cationic charge at a pH of from about 4 to about 12; provided that said suds stabilizer has an average cationic charge density of 2.77 or less units per 100 daltons molecular weight at a pH of from about 4 to about 12;

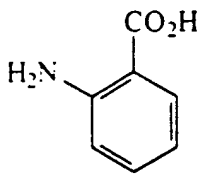
b) an effective amount of a detersive surfactant; and

c) the balance carriers and other adjunct ingredients;

provided that a 10% aqueous solution of said detergent composition has a pH of from about 4 to about 12.

positive or negative charge at a pH of from about 4 to about 12. Each R^2 is independently hydrogen, hydroxy, amino, guanidino, C_1-C_4 alkyl, or comprises a carbon chain which can be taken together with R, R^1 any R^2 units to form an aromatic or non-aromatic ring having from 5 to 10 carbon atoms wherein said ring may be a single ring or two fused rings, each ring being aromatic, non-aromatic, or mixtures thereof. When the amino acids according to the present invention comprise one or more rings incorporated into the amino acid backbone, then R, R^1, and one or more R^2 units will provide the necessary carbon-carbon bonds to accommodate the formation of said ring. Preferably when R is hydrogen, R^1 is not hydrogen, and vice versa; preferably at least one R^2 is hydrogen. The indices x and y are each independently from 0 to 2.

An example of an amino acid according to the present invention which contains a ring as part of the amino acid backbone is 2-aminobenzoic acid (anthranilic acid) having the formula:



wherein x is equal to 1, y is equal to 0 and R, R^1, and 2 R^2 units from the same carbon atom are taken together to form a benzene ring.